

# **Effect of Pre harvest Foliar Sprays of Boron and Retain<sup>®</sup> for Improvement of Quality Parameters of Apricots (*Prunus armeniaca* L.) in Tasmania**

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**A thesis submitted in fulfillment of the requirement for the degree of  
Doctor of Philosophy**

**University of Tasmania  
Australia**

**By**

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**University of Tasmania  
November 2012**

# **Dedicated**

## **To my beloved dad**

**In acknowledgement of his love, patience  
and sacrifice...**

# **DECLARATION**

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## ABSTRACT

Techniques to improve fruit firmness and quality in apricot would enhance marketability. Apricot is considered as one of the most delicious temperate fruits, and good balance of sugars and acids and a strong apricot aroma are the major determinants of exceptional fruit quality. Studies were conducted in three different varieties of apricot (*Prunus armeniaca* L.) namely 'Rival', 'Goldrich' and 'Orangered® Bhart' to determine if pre-harvest foliar applications of different concentrations of boron and ReTain® influences fruit quality and fruit yield. Firmness and sugars were of specific concern as fresh apricot has a very short shelf life of five to six days and transfer of fruit from farm to market within limited time span is a major concern. Firm fruit with adequate sweetness will allow Tasmanian orchardist to export more fruit.

The selection of the varieties for the main study was done by screening nine different varieties based on their maturity periods and availability of maximum samples. 'Orangered® Bhart' is an early harvested variety and 'Rival' and 'Goldrich' are middle harvested varieties. For this experiment, treatments consisted of four sprays of different concentration of boron in the form of Solubor (20% boron) followed by two sprays of Retain®. The pre-harvest foliar sprays were applied to trees exhibiting B deficiency as follows: (i) applied before full bloom (at green and white bud stage, and when 1-5% of flowers was at full bloom), (ii) at petal fall stage after flowering (iii) 7 days after petal fall and (iv) 14 days after petal fall. Trees sprayed with water served as controls. Boron was applied at 1.2 Kg ha<sup>-1</sup>, 1.8 kg ha<sup>-1</sup>, 2.4 kg ha<sup>-1</sup> and 3.0 kg ha<sup>-1</sup> for all varieties of apricots. ReTain® application rates were 0.40 kg ha<sup>-1</sup>, 0.65 kg ha<sup>-1</sup> and 1.0 kg ha<sup>-1</sup> and was sprayed twice (v) 7 days before harvest (BCCH scale 87) and (vi) 14 days before harvest (BCCH scale 88).

Foliar boron application improved the number of **flower clusters** by 12-15% in Rival, 2-12% in Goldrich and 4-12% in Orangered® Bhart varieties and the fruit set from 2 - 5% in Rival, 2- 8% in Goldrich and 2-8% in Orangered® Bhart variety. Thus, the sprayed trees had a greater potential to be healthy and productive with decrease in fruit drop.

All three varieties are significantly different from each other in terms of quality parameters. ReTain® eliminated the effects of Boron. ReTain® improved the firmness of 'Rival' and 'Goldrich' varieties from 10-20% and 6 – 29% respectively with decreases in sugars from 7 - 20% and 4-12%. The titrable acidity increased with the combined effect of boron and ReTain® treatments.

Boron levels at four different stages of spraying were measured with Induced Couple Plasma-Optical Emission Spectroscopy (ICP-OES). This was done in order to examine the absorption of boron in response to the foliar application. The results show increase in boron absorption of 13-48% in fruits of Goldrich followed by 13-23% in fruits of Orangered® Bhart. Boron sprays did not affect the Nitrogen (N) and magnesium (Mg) in plant tissues.

Aroma compounds are present in raw foods either as free compounds or glycosidically bound (aroma precursors). To investigate the difference in volatile constituents due to the treatment effects, the volatile compounds were investigated by means of SPME (Solid Phase Micro Extraction) using Carboxen-Polydimethylsiloxane fibers. The free aroma compounds were identified by Gas Chromatography and Mass Spectroscopy (GC-MS), finding common compounds such as linalool,  $\alpha$ -terpineol,  $\beta$ -ionone,  $\gamma$ -decalactone and 26 other compounds. Fenchone was used as internal standard. The Multivariate analysis showed a significant effect on the volatiles released from different cultivars. The amount of esters, lactones and terpenic acids released were more than carbonyl compounds. Though more than 60 compounds were eluted with SPME, 30 identified volatiles were measured in the process.

Successful development of new rural industries depends on understanding and meeting consumer needs. A study was carried out to probe consumer understanding of apricot fruit quality and their perceptions to sensory attributes. The results were correlated to instrumental measurements. Three different varieties of apricot with two different treatments of Boron and Boron + ReTain® making a total set of nine samples were used as tastings for the consumers. Apricots were harvested at a similar maturity stage according to commercial practices. Analysis and sensory assessments were carried out on equivalent fruits from uniform samples.

Despite the variability of response of assessors, significant differences were found between attributes of different treatments. Consumer preferences for some quality attributes of flavor, firmness and sugar correlated with instrumental analysis. Even though Rival is the firmest variety according to instrumental analysis, Orange red sprayed with ReTain® scored highest for overall satisfaction according to consumer preferences. These findings indicate that preharvest boron and ReTain® sprays can successfully increase apricot fruit numbers, flower clusters and fruit quality respectively.

Keyword: *Prunus armeniaca* L., Boron, ReTain®, Volatiles, SPME, GC-MS, Fruit Quality, consumer perceptions, fruit quality measurements.

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## Abbreviation

Name	Description
GC-MS	Gas chromatography – mass spectrometry
HS-SPME	Head space solid phase micro extraction
FAOSTAT	Food and agricultural organization of United Nations
FAO	Food and agricultural organization
ABS	Australian bureau of statistics
VC	Volatile compounds
ACS	1 – aminocyclopropane – 1 carboxylic acid
AVG	aminoethoxyvinylglycine
SAM	S-adenosyl-L-methionine
1-MCP	1-methylcyclopropane
EPP	Effective pollination period
ATP	Adenosine triphosphate
MDGC	Multi-dimensional gas chromatography
AAPFCO	Association of American plant food control officials
ICP-OES	Inductively coupled plasma optical emission spectroscopy
BCCH	Biologische Bundesanstalt, Bundessortenamt and Chemical industry
TA	Titration acidity
FID	Flame ionization detector
LIR	Linear retention indexes
NIST	Mass spectral data 2002
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
SSC	Soluble solids content
TSS	Total soluble solids



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# CHAPTER 1

## GENERAL INTRODUCTION

### 1.1 Apricot (*Prunus armeniaca* L.)

#### 1.1.1 History of apricot

The apricot is considered to be native to China and spread to Europe and the Caucasus (Loudon, 1838); it has been grown in China for over 4,000 years (Herbst, 2001). It now thrives in most temperate climates, including North, Central, and South America, North America, and Oceania. *Prunus armeniaca* or "Armenian plum" (also classified as *Armeniaca vulgaris*) has long been cultivated in Armenia

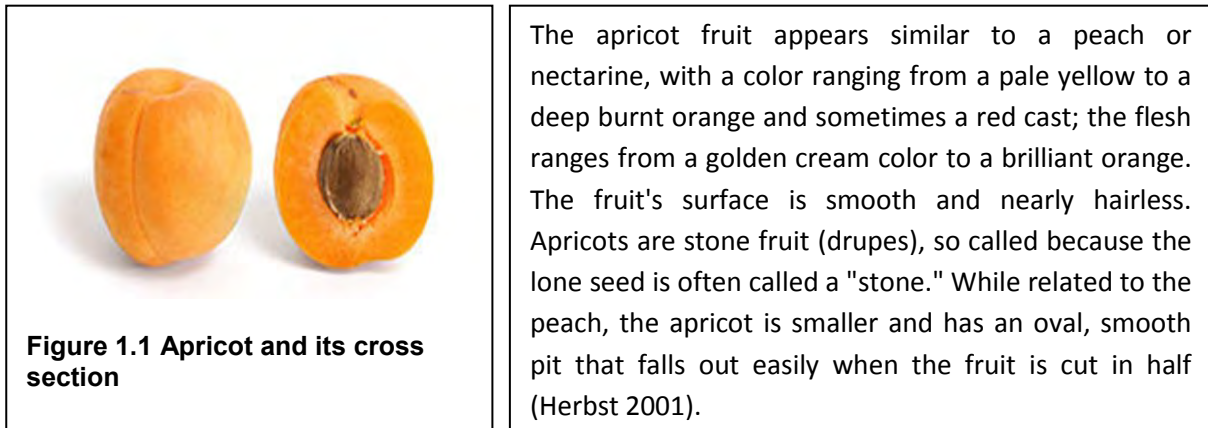
In Armenia, it was known from ancient times (6,000-year-old seeds have been discovered) and today is the main fruit culture grown in the republic (Morikian, 1983). The Roman General Lucullus (106-57 B.C.E.) even exported some trees—cherry, white heart cherry, and apricot—from Armenia to Europe. English settlers brought the apricot to the English colonies in the New World.

#### 1.1.2 Taxonomy and Description

The apricot scientific name (*Prunus armeniaca* L.) is a species of *Prunus*, classified with the plum in the subgenus *Prunophora*. *Prunus* is a genus of plant in the family *Rosaceae*. *Rosaceae* is one of the largest families of flowering plants with about 3,400 species, including apples, berries, peaches, plums, cherries and many others. The genus *Prunus* includes the plums, cherries, peaches, apricots, and almonds. The *Prunus* subgenus, which includes the apricots and plums, is distinguished from other subgenera (peaches (*Amygdalus*), cherries (*Cerasus*), bird cherries (*Padus*), etc.) in the shoots having an abortment of the terminal bud and the side buds being solitary (not clustered), the flowers being grouped one to five together on short stems, and the fruit having a groove running down one side, and a smooth stone. It belongs to subfamily *Prunoideae*.

*Prunus armeniaca* is a small- to medium-sized tree with a dense, spreading canopy 8–12 meters tall with a trunk of approximately 40 cm in diameter and a dense spreading canopy. Usually apricot's leaves are alternate and shaped somewhat like a heart, with pointed tips; they are about eight centimetres long and 3–4 centimetres wide. Its flowers are white to pinkish in color, however variability is observed among cultivars. Although often thought of as a "subtropical" fruit, the apricot is in fact native to a region with cold winters. The tree is slightly more cold hardy than the peach, tolerating winter temperatures

as cold as  $-30^{\circ}\text{C}$  or lower if healthy (Glozer and Ferguson, 2007) for north European phylum. Apricots have a recognized plasticity as a species, since they are capable of existing and producing in areas as unfavourable as the Sahara deserts as well as surviving in Canada. The limiting factor in apricot culture is spring frosts.



Apricot trees grow properly and do well in Mediterranean climate locations, since spring frosts are less severe there but there is some cool winter weather to allow a proper dormancy. Climatic adaptation is often the overriding factor determining which cultivars are grown, but preferences also relate to tolerance to pests and diseases present in different regions. Apricots prefer silt loam or sandy loam soils with good depth and drainage, but with careful selection of rootstocks it is possible to achieve good productivity on heavier and wetter soils.

### **1.1.3 Cultivation**

Apricot cultivars are most often grafted on plum or peach rootstocks. Vegetative propagation using clonal material provides the fruit characteristics of the cultivar such as flavor, size, and so forth, but the rootstock provides the growth characteristics of the plant. Apricot cultivars are very site sensitive and closely tied to specific market demands. Relatively few fresh market cultivars are considered well suited for long distance shipping and few of the apricot cultivars used primarily for processing are suitable for fresh market sales.

Pollination of apricot is seldom a problem since most cultivars are self fertile. With these cultivars, even a small population of insects will results in adequate fruit set. Apricots are normally considered self-fruitful, not requiring inter-planting with other cultivars. However, some selections, notably Vivagold, are self-sterile and provisions must be made for pollinizer varieties and pollinating insects such as bees. The three investigated cultivars present in this study are self sterile.

## 1.2 Nutritional benefits

For humans, the apricot fruits—whether fresh, frozen, canned, or dried, provide a pleasing and nutritious food source. In addition to the taste, the texture and color of apricot fruits, as well as the beauty of the trees and flowers, add to the human enjoyment of nature.

Fresh and dried apricots are high in vitamin A (as carotene). Fresh apricots also are a good source of vitamin C and K, betacarotene, thiamine, niacin, and iron. Organic acids, phenols, volatile compounds (e.g. benzaldehyde), some esters, non isoprenoids, and terpenoids also have been isolated (Riu-Aumatell, 2005; Karakaya, 2001). Dried apricots are a good source of calcium, copper, niacin, and iron. A fresh apricot of 60 grams gives 1.2 grams of dietary fiber and 18 kcal, while a 60 gram portion of dried apricots provides 14.4 grams of dietary fiber and 110 kcal (Bender and Bender, 2005). The ratios of dietary fibre and energy between fresh and dried apricots are different as the varieties used for dried and fresh fruit differ and have been selected for these specific characteristics. The highest content of soluble fibre is found in dry fruit. Dried fruit usually have more calories and natural sugars per servings because the dehydration process removes water normally found in fresh fruit. That missing water is what makes the dried form smaller than the fresh fruit, so there are more pieces of dried fruit in same serving size. The sugar found in dried fruit is mostly fructose and dextrose, the same sugar that is naturally in the fresh fruit. A large portion of the calories in this fruit comes from sugar that are externally added (USDA, 2012).

### 1.2.1 Edible uses

The apricot fruit may be eaten fresh, or pitted and dried, frozen, or canned. They may be used in desserts and for flavoring. The fresh fruit is highly perishable and seasonal (Herbst, 2001). The processed food is available in the form of jams, jellies, canned apricots, apricot juices and apricot wines.

The seeds or kernels of the apricot pits, which are poisonous until roasted, are used in confectionery and to flavor liqueurs (Herbst, 2001). Seeds of the apricot grown in central Asia and around the Mediterranean are so sweet that they may be substituted for almonds. Apricot Kernel contains 40% oil, which is composed of 30% linoleic acid and 60% oleic acid. Linoleic acid is an essential fatty acid. Essential fatty acids and their longer chain molecular products are necessary for maintenance of growth and reproduction (Eastwood, 1997). The Italian liqueur 'Amaretto' is flavored with an extract of apricot kernels rather than almonds. Oil pressed from these cultivars has been used as cooking oil. Dried apricots typically are treated with sulphur dioxide to preserve their color (Herbst, 2001).



### **1.2.2 Medicinal uses**

Various components of apricot are useful in curing different disorders in the human body. Apricot is rich in Iron along with traces of calcium, thus it is very good source to prevent anaemia. It increases the haemoglobin level in our body. High laxative content present in apricot serves as medicine for treating constipation. Cellulose and pectin helps good bowel movements by retaining water. During the time of fever, apricot juice along with honey quenches the thirst and helps in eliminating waste from the body. Various skin related diseases such as scales, eczema, sunburn and itching may be cured by apricot juice consumption.

Cyanogenic glycosides (found in seeds, bark, and leaves of most stone fruits) are found in high concentration in apricot seeds. Laetrile, a purported alternative treatment for cancer, is extracted from apricot seeds. As early as the year 502, apricot seeds were used to treat tumours, and in the seventeenth century apricot oil was used in England against tumours and ulcers (TC 2007). However, in 1980 the National Cancer Institute in the United States claimed laetrile to be an ineffective cancer treatment (TC 2007).

### **1.2.3 Other uses**

Apricot kernel oil is classed as a fat and oil, is used as an occlusive skin-conditioning agent, as well as a fragrance ingredient, and is also known as apricot kernel oil, Persic oil and Kyounin Yo oil. Dried apricot powder is used in the cosmetic industry as active ingredients of scrubs that helps in exfoliation and cleaning of the skin.

## **1.3 The apricot industry**

### **1.3.1 The international apricot markets**

With a world production of ~3.4 Mt in 2010 (FAOSTAT, 2012), apricot is the third most widely grown stone fruit crop. The production is mainly located in the Mediterranean countries that collectively account for 40% of global production. With ~14% of the world production by Turkey and the production mainly located in the province of Malatya, it is the main producer and provides ~85 % of the world's dried apricot and apricot kernels. The other main Mediterranean producers are Italy (8%), France (6%), Spain (5%), Algeria (4%), Morocco (3%) and Greece (93%). Turkey is one of the leading dried-apricot producers followed by Iran, Italy, and Pakistan. In Armenia, apricots are grown in Ararat Valley.

In United States, apricot production was about 60000t in 2010 (~2%), over 90% of which was grown in California. The remaining 10% of U.S. apricot production comes from Washington and Utah. Appendix 1 depicts the production of fresh apricots throughout the world.

China is the largest producers of fresh apricots followed by Turkey (Appendix 1). Turkey produces 20% of total world production of apricots. This includes fresh, processed and dried forms. Iran is the second apricot producer in the world with 8.2% share of total production (FAO, 2007).

### 1.3.2 The Australian apricot markets

All six mainland states in Australia have some production of apricots (Table 1). In Victoria, apricots are grown predominantly around the Goulburn Valley region, along the Murray River in Swan Hill and Mildura; whilst in South Australia fruit is grown in the Riverland region centred on the regional town of Mypolonga in the Lower Murray Region of the state. Apricots are also grown in southwest New South Wales, but they are less common in Tasmania (Figure 1.2).

Australian summer fruit (peaches, nectarines, apricots and plums) exports achieved a 20% value growth to \$30.1 million in the 2008/09 season helped by a more favourable exchange rate, and a good supply of quality fruit. The loss of the key stone fruit market of Taiwan in 2006 and ongoing strengthening of quarantine conditions for some traditional summer fruit markets has increased the urgency to seek and gain new international markets to ensure industry viability. Major export markets were Hong Kong and the Middle East with over 320 tonnes of apricots being exported to these areas in 2008/09. The main exporters of apricots in the world include France and Spain (FAO 2002).

**Table 1.1 Apricot productions by state across Australia (ABS 2008)**

	NSW	QLD	SA	TAS	VIC	WA	Total
<b>Production (tonnes)</b>	268	214	4,187	371	11,545	332	<b>16,917</b>
<b>Area (ha)</b>	78	57	371	129	702	68	<b>1,405</b>

Dominant players in the world export market for apricots include France (US\$106 million) and Spain (US\$62 million) with the world export market worth some US\$375 million (242,000Mt) (FAO 2009).



**Figure 1.2 Areas where apricot production is possible within Australia (ABS 2008)**

(Note: Maximum apricot production is in SA and Vic as shown in Table 1.1)

### **1.3.3 Apricot production in Tasmania**

The stone fruit industry covers the production of cherries, apricots, nectarines, peaches & plums in Tasmania. It is relatively new contributor to the Tasmanian agricultural sector. Apricots and cherry are the main stone fruits grown in Tasmania. Tasmania's apricot production is focused on the fresh fruit market and takes advantage of Tasmania's late season of production to enter the Tasmanian, national and International markets. Tasmania even possesses natural quarantine advantages e.g. freedom from fruit fly. The geographical isolation of Tasmania, and in particular its island status, adds significant freight costs for northbound fresh fruit.

The Tasmanian apricot industry has undergone considerable change in both production and structure since 1980. Before 1980 the industry had contracted from its peak prior to 1945, when the industry growing apricots supplied a major processor in the south of the state. The decline in production of apricots in 1980 was due to increased incidence of Brown rot disease, which led to a decline in the apricot processing industry. There is now no major processing industry in Tasmania.

Apricot is commercially grown by Qew Orchards in the Coal River Valley, the largest fresh apricot orchard in Tasmania. However, apricot growing is not widely distributed throughout the region. Apricot production is restricted to the southeast district and Derwent Valley region because of their particular climatic needs during flowering. All recent orchard plantings have been at high plant densities using varieties specific to the fresh fruit market. Tasmania's season of production for apricots is the latest in Australia. It commences early in December with the early maturing apricot varieties and peaks during January and February with bulk of apricot harvest.

### 1.3.4 Market trends

The main competition for Tasmanian apricots comes from New Zealand and Chile on both the domestic and International market (Stone Fruit Industry Review, 2007). Significant market opportunities have led to the sale of apricots through local supermarkets and sale through central domestic markets in Melbourne, Sydney, Brisbane and Perth. For overseas markets a definite opportunity exists for Tasmanian apricots in Europe, UK and Middle East. However, entry to these markets often requires storage and shipping times that go beyond the normal cool storage life of the fruit. This is particularly the case if air freighting capacity is inadequate. Additionally the use of long distance, high carbon emitting, air freight will add an environmental burden on the fruit during export that may become increasingly of concern. The trial shipment of apricots exported to the UK and has been well received. There is no major processing industry in Tasmania to absorb surplus production.

The production of apricots is likely to rise quickly as young trees planted during the last five years come into production. The following table provides estimates of apricot industry growth based on current tree numbers.

**Table 1.2 Expected industry growth, 2000-2010 for Tasmania**  
(Stone fruit Industry Review 2010)

	1999/2000			2010		
	Area (ha)	Production(t)	Farm Gate Value( \$m)	Area (ha)	Production(t)	Farm Gate Value( \$m)
Cherries	200	600	4.5	400	3000	25
Apricots	100	500	1.0	250	3000	12
Other Stone fruits	25	100	0.25	70	500	1.2
Total	325	1200	5.75	720	6500	38.2

### **1.3.5 Challenges for apricot industry**

The European markets are increasingly demanding quality assurance guarantees and food safety. The production of the food should be in a manner not detrimental to the environment along with addressing the problems related to worker health and safety and pollution control. Availability of seasonal labour for harvesting is becoming an urgent problem to resolve with the increase in production across a number of industry sectors. Providing adequate facilities for seasonal labour is also an issue.

Major weaknesses in the Tasmanian industry to be addressed are the lack of centralized marketing; achieving large volumes and continuity of supply for export markets, vulnerability to weather that results in large potential fruit losses in some seasons, lack of a major processing industry to absorb lower grades of fruit and tight availability of airfreight.

To achieve the highest consumer satisfaction fresh fruits should be picked at the peak of flavor, and eaten within hours after harvest. The goal of quality research is to achieve this consumer experience in the marketplace. Before appearing in a market display, a fruit has taken a long circuitous journey involving time and handling which may adversely affect the fruit quality. Some of the fruit are discarded at culling points within the system because of physiological disorders, handling damage, visible decay and especially short shelf life (Florkowski *et. al.*, 2009). The long time of storage may reduce consumer acceptability and at different points in the chain, quality will have different meanings. Fresh fruit quality maintenance and enhancement through ripening must occur during the chain to satisfy different quality specifications (Maya and Luz, 2004).

### **1.3.6 Importance of study**

Many factors contribute to fruit quality, ranging from functional properties to the various sensory attributes to the final enjoyment of the product. Quality is defined as degree of excellence for the requirements at that stage in the process. The consumer is influenced largely by advertising, habit, and quality, variation in use, convenience, varietal name, nutritive value, availability and of course the purchase price.

The modern apricot industry needs commercial cultivars characterized by high fruit quality attributes (Moreau-Rio, 1998). This project aims at conducting research into how to produce high quality apricots from available cultivars with; improved levels of TSS, good size and firmness, and good flesh texture while retaining excellent color, aroma and flavor characteristics. Generally, these goals are universal of apricots for any purpose.

Production of fruit with these characteristics will enhance consumer satisfaction, expand the opportunities for sale of apricots nationally, and thus have positive economic benefits as well as benefits for Australian health and benefits for the Australian industry.

## 1.4 Thesis objectives

This PhD project aims to investigate a major issue of the apricot industry by improving the quality of apricot with the help of foliar sprays at different levels of fruit maturation and storage. Fresh apricots tend to ripen and deteriorate quickly at ambient temperature, they possess short storage life of six to seven days and transport of the fruit within this limited timeframe from farm to market is major concern due to the loose skin of the fruit. Temperature management techniques at certain atmospheric gases can slow down fruit metabolism and improve their subsequent storage life

Qew orchard has a history of boron deficient apricot trees. The management practice of the orchard incorporates soil-applied boron. However, foliar boron sprays at different developmental stages of fruits have never been applied. The present study was designed after critical analysis of the boron absorption pattern over the last five years (2002 – 2007). ReTain® was applied previously at Qew orchard in a project developed for short-term crop forecasting to allow prolonged harvesting.

The previous study focused on different treatments including foliar applied fertilizers, calcium and copper, ProGibb® (gibberellic acid), Ethrel® and ReTain®. The other products used in this project failed to provide any significant changes in fruit quality or harvest date effects and were not recommended for use except ReTain®. Little experimental evidence from the field existed to aid the grower in formulating exact foliar spray timings and no scientific data was published. Previous research confirmed the use of ReTain® prolonged harvest times in apricots. Therefore, a combination of boron and ReTain® was experimented in the present trials.

Pre-harvest foliar sprays of Boron and ReTain® were applied to three varieties of apricots to improve the firmness and overall quality parameters of the fruit. ReTain® contains AVG, a known inhibitor of ACC synthase (ACS) activity (Yu and Yang, 1979) that delays the ripening process. This helps in prolonging the harvest time that allows growers to harvest the fruit from trees over a longer period. Increase in harvest time will allow Tasmanian growers to export apricot to more countries and increase their export income. The aim of this work is not limited to characterizing different varieties of apricot on their quality for fresh fruit consumption but includes their aromatic potential in order to give recommendations of appropriate pre-harvest management strategies. The apricots produced because of different treatments were analysed for consumer preferences as

improvement in overall quality will lead to consumer acceptance with the main goal of increasing fruit consumption. The Tasmanian apricot industry will have sound information to maintain and improve quality standards of apricots.

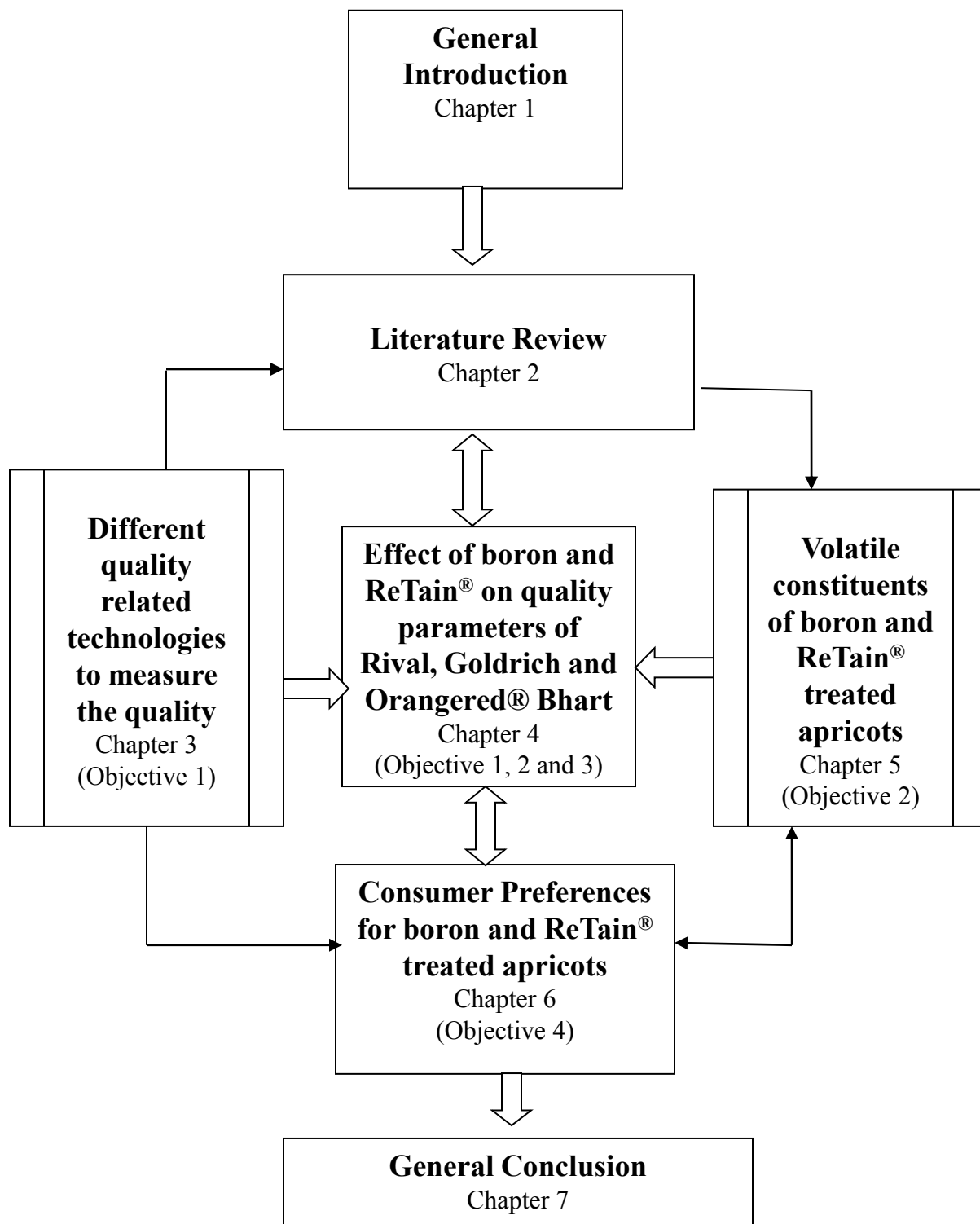
**Objective 1:** To develop a suite of technological capabilities for conducting apricot quality measurements. The measurements will be of characters that affect consumer perceptions of apricot quality.

**Objective 2:** To characterize interactions among the treatments of Boron and ReTain® across three varieties namely, 'Rival', 'Goldrich' and 'Orangered® Bhart' representative of major Tasmanian cultivars. These interactions will be characterised via post harvest changes in the physico-chemical properties and changes in volatiles due to the treatments. To compare the levels of sugars, organic acids, volatiles, B content and analyse the changes in the quality attributes to gain a better understanding of development of quality for apricot fruits.

**Objective 3:** To determine effects of boron inputs on apricot fruit and physiological status during apricot growth and development in order to give strength to the outer skin of the apricot and thereby improve the firmness of apricot.

**Objective 4:** To measure consumer satisfaction with retailed apricot quality and link back to outputs from objective 2.

**Figure 1.3 Flow diagram showing the relationships between each chapter of this thesis**



**Goal: To produce better quality apricots with foliar application of boron and ReTain®**



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Fruit development

The development of fruit including apricot can be divided into four major physiological stages following germination. These are **growth, maturation, ripening and senescence** (Gortner *et al.*, 1967) as described in Figure 2.1 (Wills *et al.*, 1998). However, a clear distinction between the various stages is difficult because transitions between the various development stages are often slow and indistinct. However, in fruits measurement of physiological (e.g. respiration and ethylene production) and/or biochemical characteristics (e.g. sugar/acid ratios) can give reliable estimates of the degree of maturity.

The apricot fruit have a triphasic pattern of development resulting in a double sigmoidal growth curve that is well described by Tukey (1934). This phasic pattern of mesocarp growth is customarily divided into four stages (Chalmers and Van Den, 1975). Within this development period four distinct phases (S1-S4) are clearly recognized. The first phase S1 is characterized by a rapid increase in cell division and elongation, and is referred to as the first exponential growth phase. In the second S2 phase, there is hardly any increase in fruit size but the endocarp hardens to form a solid stone (pit hardening). The third phase S3 is accompanied by rapid cell division resulting in an increase in fruit size; this phase is also known as exponential growth phase (El-Sharkawy *et al.*, 2007). The last phase S4 comprises the fruit ripening or climacteric phase. Stone fruit, including plums and apricots exhibit a typical double sigmoid growth pattern during fruit development and ripening (Tonutti *et al.* 1997).

Fruit maturation is the time between final growth and the beginning of ripening and senescence (Crisosto, 1994) with maturity as the endpoint of maturation. Stone fruit (including apricot) maturation and ripening are accompanied by substantial physical and biochemical changes. The visible and external changes include changes in peel color (rapid disappearance of ground color) and increase in size as the fruit nears maturity (Abdi *et al.*, 1997). Senescence occurs as a genetically programmed developmental step which consists of endogenously controlled deteriorative changes leading to death of cells, tissues, organs and whole organisms (Leopold, 1975; Nooden and Leopold, 1978). The stages of development can overlap. As indicated in Figure 2.1 all four stages of fruit development for climacteric and non-climacteric fruits are mentioned.

### 2.1.1 Growth

**Growth** involves cell division and subsequent cell enlargement, which accounts for the final size of the produce. It is an irreversible increase in physical characteristics of a developing plant or plant parts. Maturation usually commences before the growth ceases and includes different activities in different fruits (Suojala, 2000). In apricots most maturation processes are climacteric and occur after growth ceases (Valdes *et al.*, 2009) when ethylene is produced, however some, eg start of fruit yellowing occur earlier. Growth and maturation are often collectively referred to as the development phase. Senescence is defined as the period when anabolic (synthetic) biochemical processes give way to catabolic (degradative) processes, leading to ageing and finally death of the tissue.

### 2.1.2 Maturation

**Maturation** is the stage of development leading to the attainment of physiological or horticultural maturity. There is a clear distinction between '**physiological**' and '**horticultural or commercial**' maturity. It is the transient phase of development from near completion of physical growth to attainment of physiological maturity. There are different stages of maturation e.g. immature, mature, optimally mature, over mature.

**Physiological maturity** is the stage when a fruit is capable of further development or ripening when it is harvested i.e. ready for eating or processing. As mentioned Figure 2.1., it is a stage where a plant (or plant organ) has become fully developed, such as ripening in tomatoes or flowering in lettuce. This is the stage just before senescence begins. **Horticulture maturity** is the stage of development when a plant or plant part possesses the prerequisites for use by consumers for a particular purpose i.e. ready for harvest" (Watada *et al.*, 1984). **Commercial maturity** is where the plant (or plant organ) is at the particular level of development needed for the market. It typically occurs before physiological maturity. For example, tomatoes will be harvested at an early stage in the ripeness process so that by the time they reach market they are at optimum level of ripeness. However, with some products like lettuce markets wants physiologically immature produce.

#### 2.1.2.1 Maturity indices

Maturity at harvest is the most important quality criterion for a processor as it directly affects composition, quality losses and the storage potential of plant produce. The optimum harvest maturity is vital to achieve maximum post-harvest life of the fresh produce (Kader & Barrett, 2003; Kader & Rolle, 2004). Although most fruits reach peak eating quality when harvested fully ripe, they are usually picked prior to physiological maturity, to decrease mechanical injury during post-harvest handling.

Immature fruits are more subject to shriveling and mechanical damage, and are of inferior quality when ripened. Overripe fruits are likely to become soft and mealy with insipid flavor soon after harvest. Fruits picked too early or too late in the season are more susceptible to physiological disorders and have a shorter storage life than those picked at mid-season (Kader & Barrett, 2003). Harvesting fruits, including apricots, either immature or overripe can cause extensive loss of the produce; thus maturity indices are important criteria used for arriving at a correct harvesting stage.

Maturity indices vary among types, cultivars of the produce, and intended processing use. The indices used are based on (1) measurable change in visual appearance (size and shape, overall color, skin color, flesh color, presence of dried outer mature leaves, drying of plant body, development of an abscission layer, surface morphology and structure); (2) elapsed days from full bloom to harvest, and/or mean heat units during development; (3) physical changes (ease of separation or abscission layer, flesh firmness, tenderness, specific gravity or density); (4) Chemical changes (soluble solids, starch, acidity, sugar/acid ratio, juice content, oil content, tannin content) and (5) measurable physiological changes (respiration and internal ethylene concentration).

### **2.1.3 Ripening**

Ripening refers to a stage in tissue development when a fruit reaches an optimal eating quality as evidenced by favorable changes in composition, color, texture, and other sensory attributes (Watada *et al.*, 1984). The term ripening refers to a stage of fruit when it is ready for consumption. Biochemically it can be defined as the summation of changes in tissue metabolism that renders the fruit attractive for consumption by organisms that assist in seed release and dispersal. (Adams-Phillips *et al.*, 2004) The development of the fruit is completed at ripening with the irreversible process of commencement of senescence.

The fruit ripening induces structural, physical, chemical, nutritional, biochemical or enzymatical changes. These changes are (1) degradative, such as chlorophyll breakdown, starch hydrolysis and cell wall degradation (2) synthetic, such as formation of carotenoids and anthocyanins, aroma volatiles and ethylene formation (Biale and Young, 1981). Internally the sugars accumulate rapidly during ripening, sucrose being the main sugar (Brady, 1993) but glucose, fructose and sorbitol are also important with considerable variation between cultivars in sugar content and in the proportions of the four major sugars (Vitanov *et al.*, 1988).

The respiratory climacteric is associated with the burst in ethylene production in climacteric fruits such as apricots and is an important stage in the initiation of ripening (Lelievre *et al.*, 1997). The ethylene signal generated during this period triggers several

changes that lead to conversion of starch into free sugars, changes in pH, development of aroma, degradation of chlorophyll, synthesis of carotenoids and flavanoids and pulp and peel softening (Gray *et al.*, 1992; Seymour *et al.*, 1993). Thus it is known as ripening hormone.

The changes that may occur during the ripening of fleshy fruit are seed maturation, color changes, abscission (detachment from parent plant), changes in respiration rate, changes in the rate of ethylene production, changes in tissue permeability and cellular compartmentation, softening (changes in composition of pectic substances), changes in carbohydrate composition, organic acid changes, protein changes, production of flavor volatiles and development of wax on skin (Pratt, 1975).

### **2.1.3.1 Respiration**

Respiration is an indicator of metabolic activity of all living produce and plays a significant role in the post-harvest physiology and deterioration of quality of plant foods. The rate of respiration is generally proportional to rate of deterioration, which is often a good index to the storage potential of a crop. Respiration rate can be used as a criterion to compare perishability of fruits and vegetables (Muhammad *et al.*, 2001).

Fruits are divided into two classes '**climacteric**' and '**non-climacteric**' on the basis of their physiology and respiratory patterns. **Climacteric** fruits have maximum respiration rate prior to full ripening and increase in respiratory rate along with ethylene evolution just prior to senescence.

Climacteric fruits can be harvested mature and ripened off the plant. Climacteric is defined as a period in the ontogeny of certain fruits in which a series of biochemical changes are initiated by the autocatalytic production of ethylene. The period prior to the climacteric rise is referred to as the pre-climacteric phase and the respiratory activity at this stage will be at a minimum level. The period following the climacteric rise is known as senescence or post climacteric phase where there is a gradual decline in the respiratory rate. Apple, pear, peach, plum, kiwifruit, avocado, banana, mango, papaya, sapota, guava, **apricot** are examples of climacteric fruits (Kader and Barrett, 2003; Salunkhe, 1991).

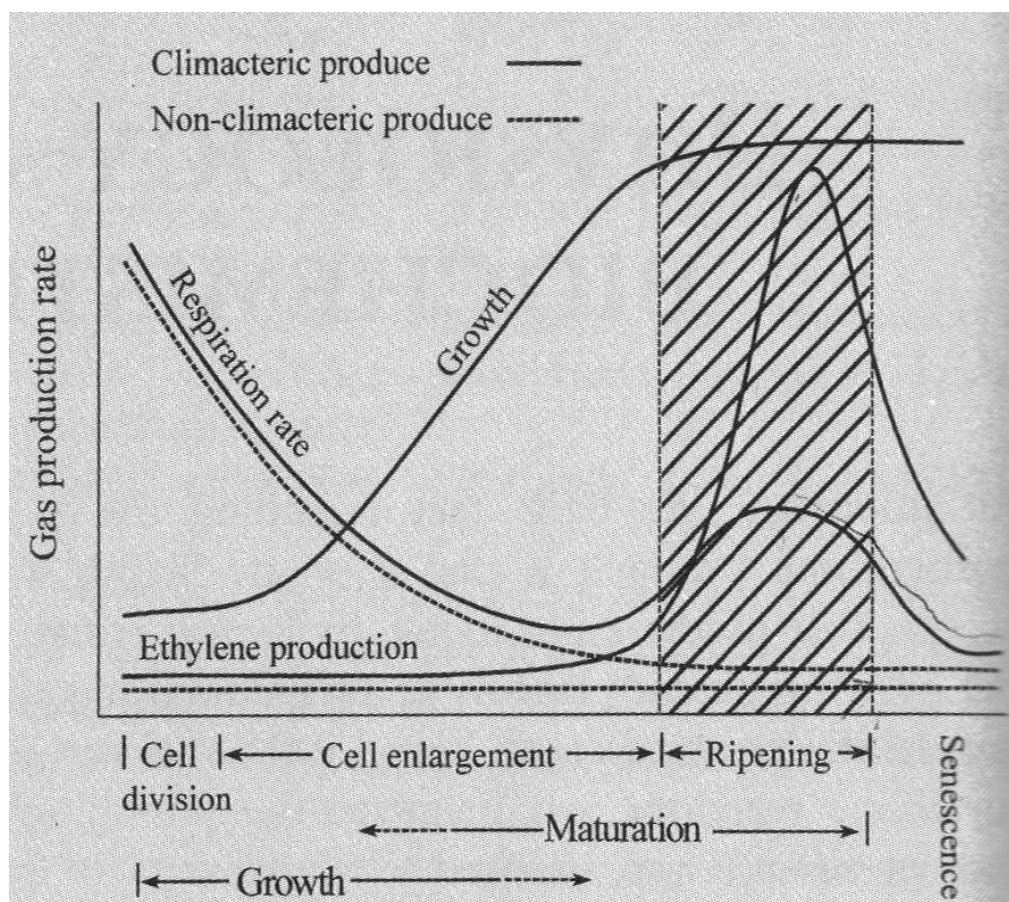
The respiration rate of some fruits does not show a climacteric rise after harvest and these fruits are best when ripened before harvest. They are grouped as **non-climacteric fruits**. These fruits ripen on the plant and are not capable of continuing their ripening process once removed from the plant (Dickson and Anderson, 1992). Thus in order to attain full ripeness and flavor, the fruits are often harvested when they are fully ripened. There is a steady fall in respiratory activity. E.g.: Strawberry, citrus fruits (grapefruit, lemon, lime, orange, mandarin), litchi, pomegranate and pineapple.

Non climacteric fruits produce very small quantities of ethylene and do not normally respond to ethylene treatment for ripening, except in terms of degreening in citrus fruits and pineapple (Kader & Barrett, 2003). Fruits are further classified according to their respiration rates and degree of perishability into very low, low, moderate, high and very high respiring commodities.

**Table 2.1 Respiration rate & Degree of perishability for different fruits**

Respiration rate & perishability	Fruits
Very Low	Nuts, dates, dried fruits
Low (<40 mg CO <sub>2</sub> /kg/hr)	Apple, pear, kiwifruit, pomegranate
Moderate (40-80mg CO <sub>2</sub> /kg/hr)	Citrus fruit, banana, cherry, peach, plum, avocado
High (80-120 mg CO <sub>2</sub> /kg/hr)	<b>Apricot</b> , fig, avocado(ripe),papaya
Very High (>120mg CO <sub>2</sub> /kg/hr)	Strawberry, blackberry, raspberry

(Source: Sudheer and Indira, 2007)



**Figure 2.1 Growth, respiration and ethylene production patterns of climacteric and non-climacteric plant organs. (Wills *et al.*, 1998)**



Ethylene stimulates ripening of climacteric and some non-climacteric fruits, synthesis of anthocyanins, degradation of chlorophyll (degreening), germination of seeds, formation of adventitious roots, abscission and senescence, flower initiation and respiratory and phenyl propanoid metabolism (Saltveit, 2002). Ethylene is used for ripening climacteric fruits such as banana (Golding *et al.*, 1999) and mango. Although ethylene does not have any strong aroma and does not contribute to typical fruit aroma, it does influence the formation of volatiles in climacteric fruits. The work of Golding *et al.* (1999) indicated that 1-MCP treated fruit showed increased ethylene production, decreased respiration rate and diminished total volatile production. The processes responsible for both increasing substrate supply and activation of ester biosynthesis system are ethylene dependant and the lower volatile yield of 1-MCP treated fruit reflects the tissue's reduced ethylene sensitivity.

In both climacteric and non-climacteric fruits, the most important aroma volatiles that increase during ripening are the esters. The characteristic or optimum flavor develops at a specific stage of the ripening process. Feijoa is a very aromatic fruit with the best aroma and flavor after natural abscission, but loses the flavor during storage (Shaw, Ellingham and Birch, 1983).

It has been observed that among a variety of climacteric (peach, plum, nectarine and **apricot**) and non-climacteric (sweet cherry) stone fruits, only apricots were adversely affected by continuous exposure to ethylene during cold storage (Palou *et al.*, 2003). Therefore the commercial adoption of methods to protect harvested apricots against the deleterious effects of endogenous or exogenous ethylene should be considered.

Apricots have a very short storage life due to a high respiration rate (Table 2.1) and rapid ripening process. The time period from commercial ripening to senescence ranges between 3 and 5 days, depending on the variety (Serrano *et al.*, 1989). These aspects force harvest of the fruit in a pre-climacteric state. Inhibition of ethylene production in "Xiaobai" apricot followed by the treatment with ClO<sub>2</sub> delayed the onset of climacteric increase in ethylene production and respiration rate. This is sufficient to extend the storage life of apricot by delaying loss of firmness associated with ripening. ClO<sub>2</sub> can block the autocatalytic synthesis of ethylene production effectively, reducing the respiration rate throughout the determination period (Zhong *et al.*, 2006).

### **2.1.3.2 Ethylene**

Ethylene is synthesized in plants from the amino acid methionine, by a series of reactions in a highly regulated pathway (Figure 2.2). ACC synthase and ACC oxidase play essential roles in this pathway. The key roles are summarized by Khan (2006) in his book Ethylene Action in Plants. Key steps in the pathway are (1) Conversion of methionine to S-

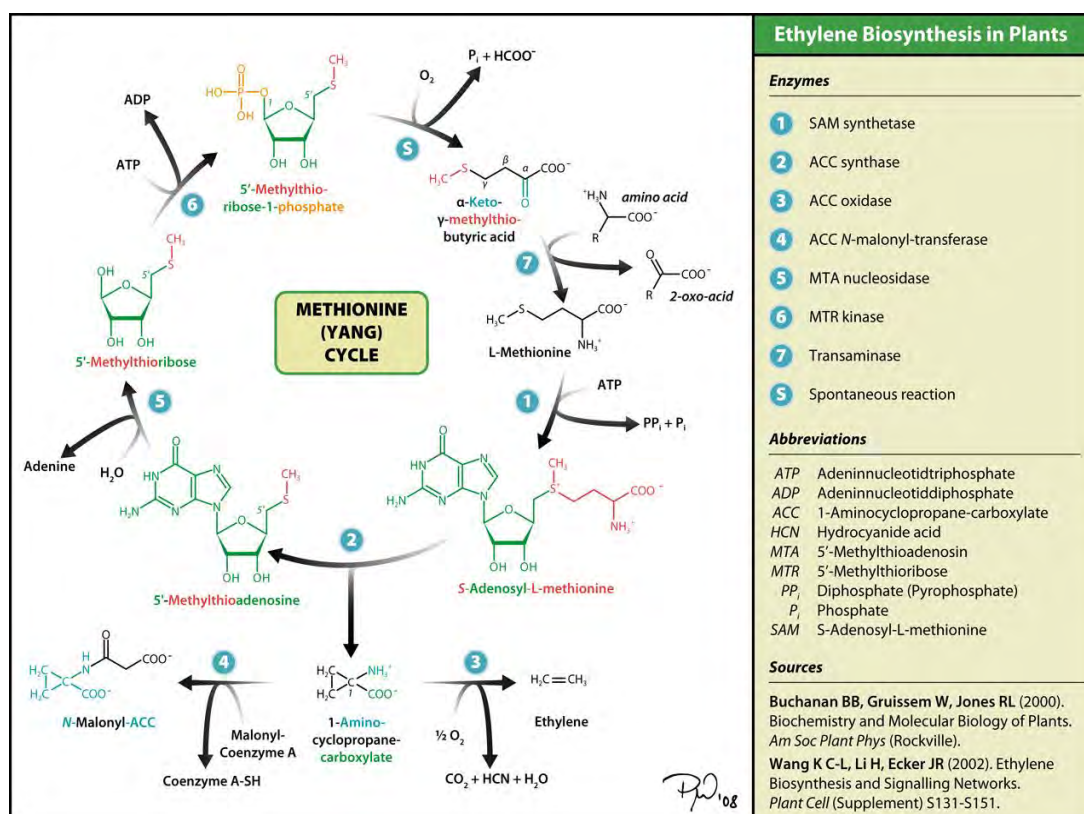
adenosyl-L-methionine (SAM) by SAM hydrolase, (2) SAM into 1-aminocyclopropane-1-carboxylic acid (ACC) by ACC synthase and (3) ACC into ethylene by ACC oxidase (Ludford, 2003; Pech *et al.*, 2003; Saltveit, 2002).

Oxygen is required for ethylene biosynthesis while both O<sub>2</sub> and CO<sub>2</sub> are needed for its bioactivity. ACC synthase is the key enzyme in the pathway leading to the production of ethylene in plants. Any one of the many genes controlling this enzyme may be responsible for the ripening action of the ethylene. Therefore it is possible to control ethylene biosynthesis without influencing other physiological processes. Genetic manipulation of these three key enzymes could be the key to controlling generation of ethylene (Garratt *et al.*, 2002; Haard, 1998; King and O'Donoghue, 1995; Wehling, 2000).

It has been suggested that ethylene dependant and ethylene independent gene regulation pathways coexists to co-ordinate the process in climacteric and non-climacteric fruit (Lelievre *et al.*, 1997). Two systems of ethylene regulation have been proposed to operate in climacteric plants. System 1 is functional during normal vegetative growth, is ethylene auto-inhibitory and is responsible for producing the basal levels of ethylene detectable in all of tissues including non-ripening fruit. System 2 operates during the ripening of climacteric fruit and during petal senescence when ethylene is auto-stimulatory and requires the induction of both ACS and ACO. The signaling pathways that bring about the induction of these two enzymes through co-ordinated regulation of ACS and ACO gene families remain unknown, although a large amount of evidence is available that indicates that a combination of both ethylene and development factors are required (Barry *et al.*, 2000)

Ethylene is a natural product of plant metabolism and is produced by all living tissues of higher plants and microorganisms. Ethylene regulates many aspects of growth and development even at a concentration as low as 0.1 ppm. Wills and Kim reported that 0.1µl/l ethylene increased softening and reduced the storage life of strawberries at 0°C and a subsequent study found a linear relationship between storage life of fruit and log ethylene concentration at 20°C (Wills and Kim, 1998). The production of ethylene by fruits and a vegetable varies substantially from, 0.1 to 100 mL/kg (Rahman, 2007).

The main sources of ethylene during marketing and retail sale are from other ripening fruit in the market, storage rooms, and exhaust of vehicles or from forklift trucks. The levels reported have the potential to cause a 10 -30 % loss in shelf life of fresh produce (Wills *et al.*, 2000). Shelf-life can be defined as “the period of time that a product can be kept under practical storage conditions and still Retain acceptable quality.”



**Figure 2.2 Ethylene Biosynthesis (Wang and Ecker, 2002)**

Ethylene can influence the post-harvest life of fruit by affecting their quality characteristics and the development of physiological disorders and post-harvest diseases (Kader, 1985). It had been observed that pulp coloration, accumulation of sugars and loss of acidity were ethylene independent processes, whereas yellowing of the rind, softening of the flesh, development of the peduncular abscission zone, aroma formation and climacteric respiration were totally or partially ethylene dependent (Bauchot *et al.*, 1998; Bower *et al.*, 2002). Similar observations were made in Charentais melons transformed with an antisense ACO from apple by Silva *et al.* and in apples silenced for either ACC synthase or ACC oxidase (Dandekar *et al.*, 2004).

Removing ethylene from storage rooms is generally beneficial in maintaining fruit quality and extending storage. Wills and coauthors suggested that the concentration of ethylene in the storage environment could be directly related to the rate of quality loss in a wide range of fruits and vegetables (Wills *et al.*, 2000) including apricots. The beneficial and adverse effects of ethylene depend on several factors such as type of produce, cultivar, and maturity at the time of harvest, temperature and activity of other hormones (Haard, 1998). The presence of ethylene sometimes has adverse effects (Optimal Fresh, 2001). The effect of ethylene is accumulative so continuous exposure to low concentration of ethylene throughout marketing can cause significant harm.



Ethylene can be removed by a number of chemical processes. Fruit softening, one of the ripening processes (Crisosto, 2003) which are sensitive to ethylene can be delayed by AVG (aminoethoxyvinylglycine), 1-MCP (1-methylcyclopropene) and 3-sachets (3 potassium permanganate sachets per box) treatments (Kader, 2000). The post-harvest life of apricots has been proved to delay with all three treatments. This delay could allow additional time for transport and marketing and may reduce physical damage to the fruit (Palou and Crisosto, 2003). The response to these treatments may vary with cultivar and maturity stage, treatment timing and characteristics and storage environmental conditions after treatment (Fan *et al.*, 2000).

A range of post-harvest technologies have developed to delay or slow ripening. These include ethylene scrubbing systems, hydrophobic storage that serves to remove ethylene and controlled atmospheres that limit ethylene production (low oxygen) or ethylene perception (high carbon dioxide). Such technologies are valuable when fruits are stored to supply an extended season and may allow transport to distant markets (Brady, 1992).

The traditional method for ethylene scrubbing is to use potassium permanganate or Purafil, which reacts with ethylene to produce carbon dioxide and water. In order to scrub the air efficiently, it is spread over as large a surface area as possible either in trays or within highly permeable bags. Potassium permanganate scrubbers are available in sachets, filters, blankets and other specialized trapping devices (Sherman, 1985). Another method for cut flowers is for their stems to be pulsed with a solution of silver thiosulfate which acts as an inhibitor of ethylene. The flowers take the solution up through their stems and this protects them from effects of ethylene.

EthylBloc® obtained in powder form, distributed in Australia by Rohm and Hass in a gaseous formulation inhibits the effect of ethylene in flowers (Sisler and Serek, 1997). It is effective at very low concentrations as low as 10 parts per billion (ppb).

The EPA has classified 1-MCP as a plant regulator, it is a gaseous organic compound that effectively blocks ethylene receptors and thus inhibits ethylene action (Sisler and Serek, 1997). In apricots, studies shows that 1-MCP delays firmness loss, decreases extent of decay and browning, improves the aroma and sometimes, depending on the maturity stage of the fruit, delays color development (Fan *et al.*, 2000). However, little is known about the physiological effect of 1-MCP on antioxidant properties of apricots. 1-MCP controls ripening induced by impact injury by increasing superoxide dismutase and peroxidase activities (Botondi *et al.*, 2003).

MCP is an extensively studied ethylene action inhibitor that has recently been shown to delay ripening and improve post-harvest quality of wide variety of fruits including pome fruits (Watkins *et al.*, 2000), citrus and tropical fruits (Porat *et al.*, 1999), strawberry (Jiang *et al.*, 2001) and stone fruits (Fan *et al.*, 2002) including **apricots** (Fan *et al.*, 2000; Dong *et al.*, 2002).

It is a cyclic olefin that blocks ethylene receptors and thus the ethylene mediated ripening process (Sisler and Serek, 1997). 1-MCP (1-methylcyclopropene) is the active ingredient of EthylBloc®. It is also formulated as SmartFresh™, a 0.14% powder for post-harvest use in fruits and vegetables. Inhibition of ethylene production by 1-MCP prolonged shelf life of apricots (Audergon *et al.*, 1999).

Aminoethoxyvinylglycine (AVG) is a naturally occurring amino acid that suppresses production of ethylene in plant tissues by competitively inhibiting 1-Aminocyclopropane 1-carboxylic acid (ACC) synthase, which is a rate limiting enzyme in the ethylene biosynthesis pathway (Boller *et al.*, 1979; Yu *et al.*, 1979).

#### **2.1.4 Senescence**

Senescence is defined as the period when anabolic (synthetic) biochemical processes give way to catabolic (degradative) processes, leading to ageing and finally death of the tissue. The distinction between horticultural ripening and senescence has never been finely drawn. Sometimes overripe mealy fruits are in the early stages of senescence.

Senescence may manifest into ripening of fruits, abscission and yellowing of leaves and softening of tissues. Senescence can be induced by common stressors such as tissue injury, deficiency of nutrients and water during production, exposure to pests and diseases and adverse environmental conditions. Induced senescence is independent of age and serves vital roles in plant defence against viral, bacterial, and fungal pathogens, controlling high levels of oxidative stress and in response to macro and micro nutrient limitation.

Watada *et al.* (1984) have defined ripening as changes that occur from the latter stages of growth and development through the early stages of senescence which result in improved characteristics associated with high aesthetic food quality. The dismantling of the chloroplast photosystem apparatus is a prominent feature of the senescence of leaves and many fruits, but it is not lethal. Senescence processes increase the probability of death by dehydration or microbial invasion for there is little evidence that senescence includes programmed death (Brady, 1973). There is evidence that a great contribution to these changes is derived from increased activated oxygen species, which are constitutively produced by normal metabolism.

A strong enhancement in the production of these radicals has been observed to take place in plant tissues during senescence processes (Thompson *et al.*, 1987; Leshem, 1988). During the period of senescence of apricot leaves, changes in photosynthetic pigment contents is correlated with the activities of some antioxidant enzymes (superoxide dismutase, catalase, peroxidase and ascorbate peroxidase). The enzyme activities and isoenzyme patterns proved to be genotype dependant (Scebba *et al.*, 2001).

Calcium and other divalent ions are useful in delaying senescence and maintaining quality of fruits and vegetables by altering respiration, protein and chlorophyll content, and membrane fluidity (Poovaiah, 1986). Sprays and dips of calcium chloride solutions delay softening and senescence of fruits by cross linking between polygalacturonide chains and calcium in cell walls, thus resulting in an extension of shelf life. In plants,  $\text{Ca}^{2+}$  ion acts as a second messenger in the signal transduction of a variety of environmental stimuli (Bush, 1995).

Three signal transduction pathways, dependant on cGMP and calcium are utilized by phytochrome to control the expression of genes required for chloroplast development and anthocyanin biosynthesis in plant cells. For example, a cGMP-dependent pathway controls chs, calcium-dependent pathway controls cab and fnr is regulated by a pathway that requires both cGMP and calcium (Bowler, 1994). Recently it has been identified that a cyclic nucleotide activated ion channel facilitates the calcium flux that initiates immune signaling in the plant cell cytosol. Elevation of cAMP is a key player in this signaling cascade (Ma *et al.*, 2009).

## **2.2 Development of stone fruit**

Flowers of *Prunus* species contain two anatropous ovules within a single carpel. One of them, a primary ovule, can be fertilized and becomes a seed; the secondary ovule usually aborts (Bradbury, 1929). Starch stored in the ovary appears to play a critical role determining the likelihood of a flower becoming a fruit (Rodrigo and Herrero, 2002).

After flowers are fertilized apricot fruit generally go through three developmental stages. The first is a rapid growth period that lasts about 30 days. Pit hardening marks the beginning of the second stage, during which fruit size increases more slowly. The second stage lasts several weeks in early maturing varieties and longer in late-maturing varieties. The final stage is the period of rapid fruit growth that usually begins 4 to 6 weeks before harvest (Connors, 1920). Apricots flower for a relatively short period of time and are often open for less than two days over each flowering period. Hence, the effective pollination period (EPP) of apricots may be short and can result in poor fruit set.

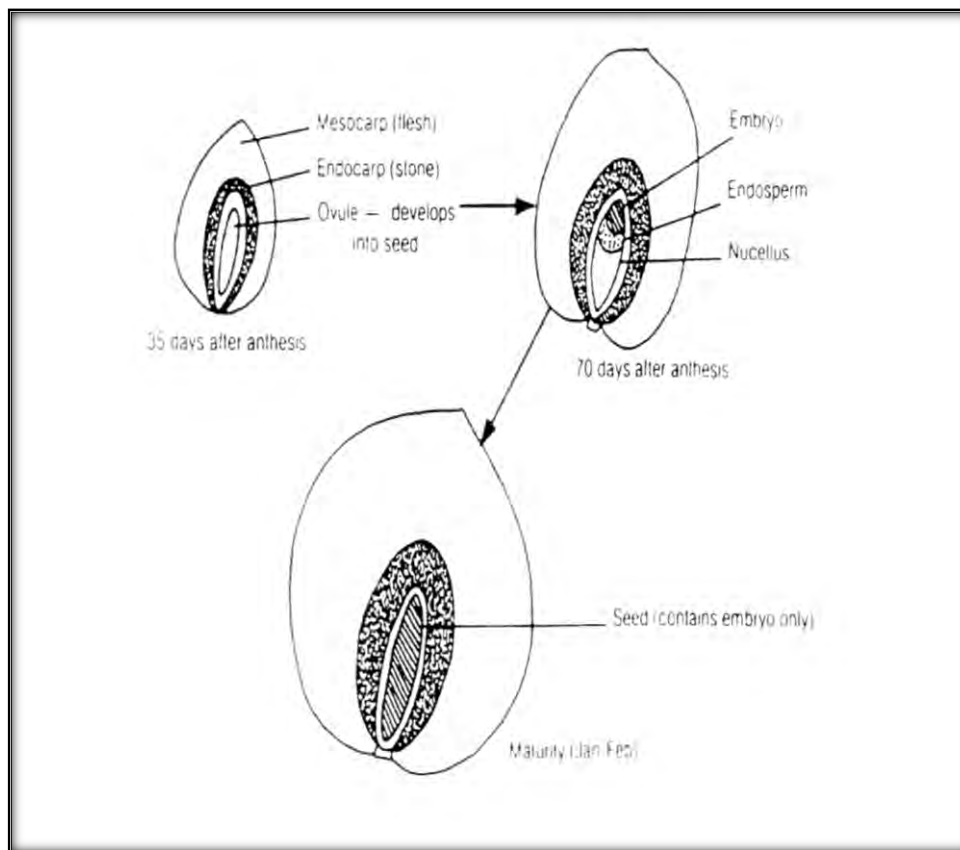
Honey bees are major agents of pollination for deciduous fruit crops including apricots (Langridge and Goodman, 1981). The time in which honey bees could achieve cross-pollination after in-hive exchange (pollen transferring from bee to bee in the hive) is short for apricots when compared to apple.

Tukey (1934) has described a distinct pattern of development for stone fruit such as apricots. Three stages of development are recognized, describing growth in terms of a double sigmoid or triphasic pattern (Jackson, 1965). In stage I, cell division is rapid and accompanied towards the end of the period by cell expansion with a rapid increase in pericarp volume, stage II is a period of relative quiescence in the pericarp and rapid development of the embryo (pit lignifications); in stage III the endocarp completes its development and the pericarp resumes a rapid increase in volume which is predominately, due to cell expansion (Figure 2.3). In early maturing varieties including those varieties with a low requirement for winter chill, stage II is compressed and endocarp closure may not be complete when the pericarp is mature (Lilleland, 1930; 1935) potentially leading to split stone.

The style and the ovary in apricot can be distinguished. It produces single seeded fruits avoiding the problems of differential fruit set associated with the number of fertilized seeds per fruit. It produces energetically dense fleshy fruits with a high flower to fruit investment and it is a histerant species where flowering take place in the absence of leaves. The gynoecium of apricot as on other *Prunus* species is unicarpellate (Sterling, 1964). The stigma of apricot is papillate and wet, and the style shows a compact transmitting tissue enveloped by vascular bundles (Rodrigo and Herrero, 2002).

Pollen grains germinate on the moist surface of the stigma within 1 day after pollination. The pollen tube penetrates into the stigma between the papillae, reaches the transmitting tissue and grows along the style in the following days. Pollen tube growth along the styles takes 3-4 days. Upon arrival at the ovary the pollen tubes traverse the obturator around 5 days after pollination, penetrate into the ovule through the micropyle and finally enter the nucleus to reach the embryo sac and achieve fertilization around 7 days after pollination (Rodrigo and Herrero, 2002).

Jackson (1965) and Jackson & Coombe (1966 a, b) reported on the development of apricot fruit in South Australia following from the work of Sterling (1935). They confirmed that growth of the mesocarp was a product of cell expansion from anthesis to 15 days after anthesis. This is similar in pattern to other stone fruit. They reported differences in cell shape between those close to the endocarp (radial expansion) versus those at the periphery of the mesocarp (tangential expansion).



**Figure 2.3 Development stages in *Prunus* species showing derivation of the full drupe from the embryo at 35 days to full maturity at 130 days. (Source: Jackson, 1974.)**

Maturity and ripeness are reported to be important predictors of browning in fruit that are dried. (McBean, 1950; Dahlenburg, 1976). Enzymatic browning results from oxidation, in the presence of oxygen, of phenolic compounds by polyphenol oxidases. The phenolic compounds are oxidized to quinines, which then polymerize into brown products (Amiot *et al.*, 1997). The tendency of fruits to brown results from the action of many factors, which vary with age of the fruit, physiological stage, cultivar, disease and the treatments to which they are subjected (Macheix *et al.*, 1990). Because there is increasing demand for apricot products with traditional orange color (juices, purees, jams, pre-cut apricots) cultivars with little browning are cultivated.

Desired product appearance is principally achieved through cultivar selection (Kays, 1999). The cultivars can change according to consumer demand, but it is important that they satisfy the grower and processor requirements to guarantee a quality fruit. Effective control systems are necessary to eliminate low quality fruit and to motivate the growers through financial incentives to produce high quality fruit, because quality factors influence the marketplace value (Collins, 2006).

## 2.3 Fruit quality

Quality is a term frequently used but rarely defined (Shewfelt & Bruckner, 2000). The term quality is defined as any of the features that make something what it is, or the degree of excellence or superiority. Quality is defined as the sum of all subjective and objective parameters of a product comprising external properties, nutritional quality and processing quality (Schupan, 1961). Other post-harvest horticulturist define quality as a combination of attributes, properties or characteristics that give each commodity value in terms of its intended use (e.g. raw, cooked or processed) which varies among producers, traders and consumers (Kader, 2001)

However, the word quality is used in various ways for fresh fruits and vegetables such as market quality, utilization quality, sensory quality, nutritional quality, and ecological quality, external and internal quality, shipping quality (Kader, 2002). The definition is different for the producer, shipper, canner and the consumer. The marketing of fruits is aimed eventually at appealing to the consumer for who previously learned criteria play a major role in determining acceptability. The purchasing habits of people are typically conservative so that an inducement is often required to get people to experiment with different fruit characteristics such as pears with red skin. However, these visual differences may serve the purpose of sellers seeking greater sales volume as external factors might be considered of paramount importance in consumer recognition and decision making.

The main role of post-harvest technology is to devise methods by which deterioration of produce is restricted as much as possible during the period between harvest and end use and to ensure maximum market value for the product. This will often require maximum market opportunities e.g. long life and minimal quarantine issues to reach all possible markets.

A number of pre-harvest cultural practices can influence post-harvest quality and performance. There are also many handling practices during harvest, packing and distribution that affect quality, as well as potentially deleterious effects of various fruit deterioration problems. While post-harvest horticulturists have generally focussed on harvest maturity (Kader and Mitchell, 1989a) and temperature management (Mitchell, 1987; 1989) as their starting points, many earlier decisions taken in the orchard will profoundly influence the post-harvest quality of the fruits.

Quality criteria including those for apricot can be divided into extrinsic (e.g. price, brand, nutritional information, product information, country of origin) and intrinsic factors (e.g. appearance, color, size, shape).

Some important quality criteria for consumers are appearance, size, color and shape, surface and internal defects, mouth feel or texture, flavor and nutritional value.

Measures are often taken to improve the external visual quality such as waxing of apples, degreening of oranges, orange-colored mesh bags to reinforce the color of oranges etc. However, with poor internal quality, sometimes consumers are disappointed and this leads to a decrease in repeat purchases. For example consumers are often disappointed by the poor organoleptic properties of early season fruit (e.g. immature nectarines that fail to ripen properly) or out of season fruit (e.g. mealy apples that have been over-stored). The intrinsic quality parameters, combined with knowledge of the consumers segment's perceived extrinsic quality attribute requirements, is currently suggested as the preferred method of meeting consumer expectations of products (Lundahl, 2006).

The official standard of apricot quality relies on the fruit calibre. Physico-chemical requirements are regularly established for every new variety (Lurol *et al.*, 2007). Proper determination of apricot fruit quality overcomes the problem of sampling in fresh apricot production.

Apricot quality is particular variable depending on the variety, geographical origin, environmental factors and location of fruit on the tree. The influence of these factors in the orchard consequently creates significantly variability at harvest time, making the organization of fruits in homogenous batches difficult (Audergon *et al.*, 2006). Therefore, a need for proper determination of apricot quality for each fruit is essential.

### **2.3.1 Appearances**

A rapid visual assessment can be made on the basis of size, shape, color, condition (such as firmness), and presence of surface defects or blemishes. Size can be measured by circumference, diameter, length, width, weight or volume. Many fruit are graded according to size, often by diameter measurement, with similar sizes of fruit being packed together to facilitate marketing and retail sales (Wills *et al.*, 1998).

It is also possible that by keeping single sizes together consumers lack an external reference and minimize preference for specific size. While the appearance factors of shape and form are considered to be generally of minor influence in the consumer evaluation of quality, size is an important quality determinant related to the end use (Kays, 1999).

### 2.3.2 Shape and size

Shape is a criterion that often distinguishes particular cultivars of fruits. Characteristic shapes are usually demanded by the consumers, who will often reject a commodity that lacks the characteristics shape.

One of the hallmarks of fruit crop domestication has been an explosion in fruit shape variation (Nothmann, 1986; Smart, 1995) and it determines the market of fruit-bearing crops. For example, the fullness of cheeks adjacent to pedicel may be used as a guide to maturity of mango and some stone fruits such as apricots (Dhatt and Mahajan, 2007). The shape was differentiated as round, elliptical or oblong visually. Despite its historical and economic importance, the molecular basis for fruit shape variation is largely unknown. Pear shaped fruit is one of the most recurring shape themes (Liu *et al.*, 2002). Other options are flattened, toroidal shaped peaches that are both recognisable and may be preferred in their own right e.g. Angel peaches.

Fruit shape is used for cultivar descriptions in applications for plant variety rights or cultivar registers (Beyer *et al.*, 2002), evaluation of consumer preference, investigation of heritability of fruit shape traits (White *et al.*, 2002), or analysis of stress distribution in the fruit skin (Considine and Brown, 1981). Knowledge of size and shape is important in screening solids to separate foreign materials and in sorting and sizing of fruit.

Uniform and characteristic shape is an important quality characteristic. Misshapen products may be more susceptible to mechanical injury and are generally avoided by consumers. Another example where shape is important is for broccoli. For the fresh market, compact broccoli florets are desirable while for fresh-cut, space between the florets is important to allow for cutting without injury.

Size of product can also be important depending on its intended use. Consumers tend to associate large size with higher quality and view large fruit as more mature (Mitcham *et al.*, 1996). This can however, be highly market specific or end use specific and translate into different desired values in specific markets e.g. The 'Cripp's Pink' apple, a Western Australian bred variety, is highly popular because of its distinctive pink blush on a apple green background, crisp texture, and high sugar-acid ratio (Mackay *et al.*, 1994).

The physical properties of apricots are important for the design of equipment for harvesting and post-harvesting technology, transporting, sorting, cleaning, separating, sorting, sizing, packaging and processing it into different food. Maturity of fruits can be assessed by their final shape and size at the time of harvest. Size is often specified as a quality standard with large size generally indicating commercial over maturity and under sized produce indicating an immature state.



Size and shape are considered as important factors for determining the quality attributes of the apricot. It can be measured with simple instruments such as digital callipers (Bianco *et al.*, 2010) or with hi-tech instruments such as Instron Universal Testing Machine (DeMartino, 2002) and Area Measurement systems Delta-T (Jannatizadeh *et al.*, 2008). A digital calliper is used for our experiments and the detail of the procedure will be discussed in Chapter 3.

### **2.3.3 Color**

Color is often the main parameter of all the appearance attributes considered by consumers when choosing a product, as consumers have expectations of overall quality based on color, such as color cues for banana ripeness (Frank *et al.*, 2001). Consumers associate colors with freshness, better taste, flavor and ripeness. Fruit palatability increases during ripening due to flesh softening, the disappearance of bitter, astringent, or sour compounds and a concurrent increase in sugars. Concomitant color changes during ripening may provide an indication of fruit maturity and thus palatability, eating quality and nutrition (Wills *et al.*, 2007). In fruits such as apples, cherries and strawberries there has been much interest in breeding fruit varieties with different colors, hues, and patterns with changes often controlled by total anthocyanin content. Red skin apples are preferred to other color apples (Leonard and Wadsworth, 1989).

Green to yellow color change due to preferential chlorophyll degradation appears to be a reliable indicator of ripening in various fruits. Color can affect or reflect the taste, odour, preference and acceptability of food items. Taste and flavor intensity generally increases with increasing pigmentation.

Internal maturity and eating quality is not always reflected or well aligned with peel color. For example, some orange cultivars are at their optimum flavor and quality when they are green and not orange as normally consumers perceive. In some fruits, peel color is manipulated in order to ensure that internal maturity and quality is unlinked to appearance of the peel or that fruit color matches the preference of consumers (e.g. limes, lemons and oranges being green, yellow and orange respectively) (Janick, 2010).

Mangoes are picked green and reach their characteristic yellow to orange background color on the shelves. Green ripe mangoes ripen internally, but their peel does not change during shelf life (Jacobi *et al.*, 1998). Achieving and maintaining uniformity of expectations along the chain for visual characteristics in the industry is important to ensure equity and harmony.

Total carotenoids contents in Spanish cultivars of apricots and breeding materials were assessed by Ruiz *et al.*, (2005b) and a close correlation between carotenoids content and the color parameter, hue angle was reported. Digital images were analyzed using an algorithm, that converts images from RGB to CIE 1976 L\*a\*b format, extracts the fruit image and quantifies color characteristics.

For effective visual assessment, multiple variables such as spectral quality, intensity and angular size of the light source should be controlled. The direction of the light, observer's spectral response and distance between the specimen and observer are also of critical importance. The produce should attain proper shape and size. Medium size apricots are generally preferred by the consumers, because they tend to view large fruits as over mature. The appearance of the product is the most important critical factor in the initial purchase while subsequent purchases may be more related to texture and flavor of the previously purchased fruit.

Consumers usually purchase firm apricots and ripen them at home. Most apricots have a reddish blush, but the important color is the yellowish orange that dominates the surface of the fruit. It is also important to note that some varieties of apricot ripen from inside out like pears and tomatoes. Many consumers eye the small size and green color and pass them by in market. However, knowledgeable shoppers know that they are the best eating apricots and superb for jams and desserts.

### **2.3.3.1 Color Measurements**

To ensure uniformity of practice among inspectors, visual aids for inspection e.g. color charts, models, diagrams, photographs are used whenever possible (Kader, 2001). The evaluation of digital images by consumers in different markets can help breeders and marketing agents direct produce with the appropriate external quality cues to selected markets (Cliff *et al.*, 2002).

Colorimeters provide, at a higher cost, an objective measurement, but usually of a localized area. Software packages have been implemented to perform evaluations of the fruit surface (e.g. detection of fruit blemishes) but none of these methods were successful in performing large surface areas automatically, on large sets of images. More recently, new image processing tools to measure color have been developed and are readily available which enables the measurement of average fruit color from digital images. (Darrigues *et al.*, 2008; Talias *et al.*, 2008). For example, apples, tomatoes, stone fruits and citrus fruits are routinely graded and sorted with machines of Color Vision Systems (CVS), Victoria.

Multiple color spaces can be used to define color. The CIE L\*a\*b\* (CIELAB) is a color space specified by the International Commission on illumination. Gloss is a visual aspect of quality that depends on the ability of a surface to reflect light. Products that are freshly harvested often have a bright, glossy surface and this appearance factor can be greatly reduced with weight loss and other post-harvest handling conditions. Alternatively it can be increased artificially by waxing fruit. There are small portable instruments from Minolta and BKY Gardener for measurement of gloss.

In apricots, spectra were directly acquired, in reflectance mode on whole fruit using non-destructive methods of Visible-NIR spectrometer (Costa *et al.*, 2006). Moreover, destructive methods using Minolta Chromatometer, portable tristimulus colorimeter (Drogoudi *et al.*, 2008) is also used. The calorimetric method was previously applied with conclusive results to characterize many fruits such as peaches, nectarines and apricots (Dixon & Maehama, 1998; Chahine *et al.*, 1999).

#### **2.3.4 Firmness**

Texture is an important attribute of fresh fruit; many of these products are desired for their crispy or crunchy characteristics, but others are appreciated for their juicy, soft and easy to chew and swallow characteristics (Roininen *et al.*, 2004). Instrumental measurements of fruit texture are common and desirable in industry and research because they reduce variation in measurement and provide an exact output measure that is able to be interpreted (Abbott, 1999). Thus, the horticultural industry defines textural quality by instrumental firmness measures.

Fruit firmness is one of the most important quality variables; it is an indirect measurement of ripeness and its accurate assessment allows appropriate storage periods and optimum transport conditions to be established. Texture is defined as a sensory attribute and can only be measured directly by sensory means (Brennan, 1984). Firmness is a quantitative concept; it is only a small part of the sensation of texture in the mouth.

Szczesniak, (1963), proposed a classification of food textures based on rheological principles, which could be monitored by both instrumental and sensory methods of characterization. This author classified the textural characteristics of food into mechanical and geometrical properties. The mechanical properties were subdivided into five primary variables (hardness, cohesiveness, viscosity, elasticity and adhesiveness) and three secondary variables (brittleness, chewiness and gumminess).

The geometrical characterization was divided into two general groups those related to the size and shape and orientation. Moisture content, oiliness and greasiness were other characteristics of texture characterization (Garcia-Ramos *et al.*, 2005).

Fruit texture is described by sensorial terms such as crispness, juiciness, grittiness and flouriness. Instrumental measurements, however, define the mechanical properties of fruit tissues in terms of force, pressure and energy. The ability to sort by firmness would help to obtain a more uniform pack of consistent high quality fruit and facilitate more timely marketing ( Blahovec, 2002; Wang, 2004 ; Chauhan *et al.*, 2003).

#### **2.3.4.1 Different techniques used to measure firmness**

The methods used to measure firmness include subjective evaluations such as assessing the results and force needed in squeezing between finger or hand, pushing a thumb into flesh, biting and chewing or by objective measurement using the penetrometer generally refers to as Magness-Taylor (M-T) or Effe-gi test (Wills and Tirmazi, 1982). Penetrometers and Instron Universal tester (Holt, 1970) are examples of destructive devices as they puncture the fruit during measurement.

In the early 20<sup>th</sup> century firmness was measured with a marble partially embedded in paraffin resting on a scale and the amount of force required to penetrate the fruit was measured (Morris, 1925). A more elaborate instrument was developed, in which a cylindrical plunger was used with a lever and depth of penetration was controlled by electrical contact (Lewis *et al.*, 1919). These principles were later used by Magness and Taylor (1925) to devise a portable tester for apple, peach and pear. The Magness-Taylor firmness was used in fruit because of the acceptance of this measurement in the handling, processing and storage operations. The Magness-Taylor firmness is a measurement of the crushing and shearing strength of the tissue and not of its elastic properties, while the stiffness coefficient is thought of as an elastic property index (Armstrong, Zapp and Brown, 1990; Duprat *et al.*, 1997).

As these traditional methods are destructive, non-destructive techniques for measuring firmness have been extensively investigated. Recent developments in non-destructive firmness testers, measure fruit deformation under applied force, includes a thumb sensor (Mizrach *et al.*, 1992), bench top-type (Yakushiji *et al.*, 1995), hand-held meter (Takao and Ohmori, 1994) and mechanical sensor (Lesage and Destain, 1995).

Bench top type fruit firmness is scored between 0 and 100, based on the deformation of the fruit under a specific load. The deformation is restricted to the elastic range so that no bruising occurs. The bench top firmness tester ("HIT Conter"), is equipped with a computer control and data acquisition system, it is suitable for firmness measurement of fruits such as kiwifruit, mango and persimmon; its loading rate and applied force can be adjusted as required. The hand held firmness meter ("Handy HIT") was developed mainly for measuring kiwifruit firmness. The meter is equipped with a spring to provide constant load, and the firmness score is read from the dial gauge, reflecting measurement of the fruit deformation (Abbott, 1999).

A mechanical sensor was designed to measure the firmness of tomatoes, which consisted of a small plunger constrained to penetrate slightly into the fruit by accurate lever mechanism. All these devices were designed for use in packing sheds or in storage facilities for repeated measurements over time, such as during ripening, without causing substantial damage to the fruit.

A non-destructive firmness measurement method for soft fruits such as peach and apricot was reported, in which a ball was pressed into the fruit with constant force and deformation was measured (Bellon *et al.*, 1993). Non-destructive measurements of fruit softening under an applied force have been achieved with the relatively inexpensive Analogue CSIRO Tomato firmness meter (AFM) (Brady *et al.*, 1983; Sumeghy *et al.*, 1983). This compression meter was initially developed by Peter Rutledge, Barry McGlasson and Bill New at the CSIRO Division of Food Research, Queensland, Australia. Alternatively, more elaborate electronic systems, such as one which incorporates a data logger to record the firmness measurements may be used.

Some promising dynamic methods for fruit quality evaluation were based on measurement of fruit response to force vibration and acoustic response. Most of them applied a frequency analysis technique to sound signals by means of a microphone. It was observed from this research that resonant frequencies decreased with ripening. Nevertheless, to my knowledge, dynamic excitation methods by microphone have not yet been successfully adapted to the sorting line except in apple. This is mainly because of insufficient sorting capacity or implementation difficulties (Wang, 2004).

Usually, apricot firmness is calculated in a destructive manner by means of the Magness Taylor test (Magness and Taylor, 1925; Barreiro, 1994), penetrometer (Azodanlou *et al.*, 2003) and stress relaxation (Kojima *et al.*, 1991; 1994). The technique of Magnus Taylor is well accepted and used for classifying fruit by many packing companies and quality

laboratories. For our experiments we have used a penetrometer. Penetrometer firmness has been suggested as a standard for determining maturity in stone fruit, and in particular, over-maturity (Crisosto, 1994). The detail usage of instrument is discussed in Chapter 3.

Technical advances have led to the development of non-destructive devices capable of measuring fruit internal variables. Three basic methods have been explored: 1) measurement of sound amplitude propagated through a fruit (Nybom, 1962), 2) resonant frequency (Abbott *et al.*, 1992; Falk *et al.*, 1958; Finney, 1970) sound velocity (Garrett and Furry, 1972).

Firmness of apricot is also measured by Laser air puff detector which uses a brief puff of compressed air to deform the product surface about one millimetre. The laser displacement supplies a quick and accurate measurement of deformation (McGlone and Jordan, 2000). Application of an acoustic impulse response method is reported for the evaluation of apple, mango and apricot (Petrisor *et al.*, 2010).

### **2.3.5 Defects**

Normal appearance is extremely important in the marketplace. Consumers have a firm idea about what constitutes normal appearance, and any deviation will be considered a defect. For example wilting of leafy vegetables is an obvious defect and therefore unacceptable to the consumer. Although a premium price may be obtained for produce that is free from blemishes, there will still often be a market for lower grade produce (e.g. through roadside stalls, lower price outlets, pulping grades, or as a specialist product e.g. unsprayed).

Textural defects and interaction of flavor and texture are more likely to cause rejection of fresh product (Harker *et al.*, 1997). The acceptability of commodities differs between countries and between different regions within a country. For example in Japan, only netted melons without ground spot are in demand in Japanese markets. Bruising, surface discoloration, softness and decay are the most common defects of apricots, along with sunken discolored areas. Stone burn in **apricots**, commonly called pit burn **defect**, is when the flesh around the **apricot** stone turns brown and softens. Failure to sort and discard immature, overripe, undersized, misshapen, blemished or otherwise damaged produce creates problems in the subsequent handling and marketing of the produce (Wills *et al.*, 1998).

### **2.3.6 Mouth feel**

Mouth feel including texture is the overall assessment of the feeling a food gives in the mouth. It is a combination of sensations derived from the lips, tongue, and walls of the mouth, teeth and even the ears. Each of these areas is sensitive to small pressure differences and responds to differences and responds to different attributes of the produce. Lips sense the type of surface being presented. Teeth are involved in determining the rigidity of structure.

The tongue and the walls of the mouth are sensitive to the type of particles generated following cleavage by the teeth. Ears sense the sounds of the food chewed intimately complementing mouth feel. The cumulative effect of these responses creates an overall impression of the mouth feel of the produce (Wills *et al.*, 1998).

### **2.3.7 Flavor**

New cultivars of fruits with better flavor and nutritional quality are being and will likely continue to be developed using both biotechnology and plant breeding methods, especially for commodities for which easily monitored markers for good flavor and nutritional quality are identified (Kader, 2008). Flavor is a complex, multigenic trait providing unique challenges to breeders and has been a high priority in recent years. Selection for yield, fruit size and shelf life characteristics in particular have had unintended negative consequences on fruit flavor (Goff, 2006).

Fruits flavors depend on taste and aroma. Taste is the detection of non volatile compounds by several types of receptors in the tongue. Aroma is related mainly to sugars (fructose, glucose and sucrose), salts, acid (citric, malic and tartaric), bitter compounds (alkaloids, flavanoids) and volatile components e.g. alcohols, esters, aldehydes, terpenes, lactones, carbonyl compounds etc. Although taste and aroma are well integrated in their contribution to the overall flavor, aroma is often considered to play a dominant role in flavor (Baldwin, 2008; Goff, 2006 and Voilley, 2006). Thus, future research on flavor quality must include both non-volatile and volatile constituents that contribute to taste and aroma of fruits.

Sugar–acid balance and contents are primary determinants of the taste attributes of fruit, and so are of major significance for consumers. Too much acid and the fruit is tart and unpalatable; too little and the fruit is insipid and bland. In horticultural terms, acid levels are often expressed as titratable acidity (TA), and this is used as one indicator of taste. Another indicator used is the refractive index of the expressed sap (recorded as °Brix). This is a measure of the soluble solids concentration (SSC %) of expressed juice and represents the sum of organic acid, salts and sugar contents. Several organic acids may be present, but

certain ones are characteristic of particular species or cultivars. For example, malic acid predominates in pipfruit (pomefruit), citric acid is dominant in citrus, while tartaric acid is dominant in grapes.

High priority is given to replace poor flavor cultivars with good flavor cultivars from among those that already exist or can be made by selecting new varieties with superior flavor and good textural quality. Some post-harvest agriculturists think that the bottom line for flavor quality is still genetic. Breeders need analytical tools in order to select for flavor quality. Use of molecular markers that relate to flavor may help to identify important enzymes in flavor pathways (Baldwin, 2008).

The need for the production of fruit genotypes with better flavor can increase their consumption with better consumer acceptance and great economical benefits. This means fruits will have high sugars and moderate acids, low phenolics and enough of the desirable odour active volatiles for good aroma. Since flavor quality involves perception of the tastes and aromas of many compounds, it is much more challenging to manipulate than other quality factors. This may be the reason that improvement of flavor quality has received less attention from biotechnologists so far than the textural quality of fruits (Vicente *et al.*, 2006). There is also unlikely to be one preferred flavor as different people and cultures have different preferences for optimal balances of fruit flavor attributes.

Soluble sugars and organic acids, contribute indirectly to phenolic metabolism by altering pH and through use as building blocks for phenolic compounds (Perkins-Veazie and Collins, 2001). An excellent overview of developments in flavor science and their implication for the food industry, including characterization of aroma compounds, flavor retention, release of flavor components from food matrix and influences on flavor perception is given in an edited version of the book by Voilley *et al.* (Voilley and Etievant, 2006). Continued research is needed to match aroma sensory and instrumental data and to elucidate texture-aroma interactions and odour-taste interactions in flavor perception.

Several to hundreds of volatile and semi volatile compounds may be responsible for the characteristic aroma of a fruit. Some of these essential compounds will be present in minute concentrations (parts per billion) that require expensive and complex analytical equipment. To determine exact volatile components actually impacting the flavor of a fruit requires methods dependant on gas chromatography (GC) or gas-chromatography/mass spectroscopy (GC-MS) separation, gas chromatography/olfactometer (GC-O) or compound separation linked to sensory analysis which again are complicated, labour intensive and expensive procedures.



Although non-destructive methods to measure quality using acoustical and near infrared systems have led to their commercial use to select fruits with acceptable flavor quality, there is a need for continued development of non-destructive sensing of flavor quality. This should include sensing the degree of freshness, use of near infrared spectrophotometry to estimate concentrations of flavor-related, non-volatile constituents; use of aroma sensing technology such as the electronic nose to detect desirable and undesirable aroma volatiles and taste sensing technology like electronic mouth or tongue equipment (Li *et al.*, 2006). Flavor detection, importance and considerations are often overlooked within the industry due to practicality.

Flavor volatiles in fruits arise from numerous biosynthetic pathways (carbohydrates, amino acids, fatty acids, oxidations and  $\beta$ -oxidation) and include a wide range of molecular weight alcohols, aldehydes, esters, furanes, glucosinolates, ketones, lactones, nitrogen and sulfur containing compounds, terpenes and other compounds. Volatile esters often make the major contribution to impact aromas in fruits such as apple, banana, pear, strawberry and melon. Flavor loss during fresh-cut storage can proceed as a direct consequence of senescence and may be driven by catabolic, metabolic and diffusional mechanisms (Beaulieu, 2007; Forney, 2008).

Apricot fruits are greatly appreciated for their pleasant and delightful aroma, which contributes to determine the apricot fruit quality (Vanoli and Visai, 1997). Aroma is a major quality component that distinguishes apricot from other stone fruits such as plums and their interspecific hybrids, because it is developed by a large number of distinct volatile compounds (Gomez *et al.*, 1993). More than 100 different aroma compounds are present in apricot fruit. A recent survey has confirmed the importance of apricot flavor to the consumer, generally showing a direct impact on consumer acceptance (Azodanlou *et al.*, 2003).

Recent work on apricot flavor have focused on refining extraction techniques for volatile compounds (Chen *et al.*, 2006; Peytavi *et al.*, 2006; Calderón-Santoyo *et al.*, 2007) as well as changes in volatile during fruit development (Gómez and Ledbetter, 1993) and storage (Defilippi *et al.*, 2009). The aromatic quality of the apricot increases during its ripening process and is associated with ethylene production (Song and Bangerth, 1996; Singh *et al.*, 2004). Certain aromatic compounds can also be utilized as molecular tracers to discriminate apricot varieties (Rodriguez *et al.*, 1980).

Despite the number of studies characterizing aromatic changes during fruit ripening (Song and Bangerth, 1996; Gomez and Ledbetter, 1997) and some evidence of better fruit quality (higher sugar/acid ratio) in late ripening cultivars (Martínez-Calvo *et al.*, 1998;

Audergon *et al.*, 2001; Vemmos *et al.*, 2008) no work is done to observe the association of aroma composition and ripening season, which might contribute to improve fruit flavor in late varieties.

A technique suitable for the analysis of flavors in food must be able to isolate all relevant aroma compounds with good recoveries while the formation of artifacts should be avoided or, at least, limited as much as possible. Next to isolation, the most important aspect is the identification of the food constituents which contribute to aroma. These are usually present in trace to ultra-trace amounts and comprise a wide range of classes of chemical compounds (Blank, 1997).

### **2.3.7.1 Previous studies on apricot flavor**

- The first significant studies on apricot flavor were performed by Tang and Jennings (Tang and Jennings 1967; Tang and Jennings 1968) who utilized direct extraction, vacuum steam distillation, and charcoal adsorption to isolate the volatiles from Blenheim variety.
- A number of terpene hydrocarbons, terpene alcohols, and lactones were identified by gas chromatographic retentions and infrared spectroscopy. (Rodriguez, *et al.*, 1980). He studied the variety Rouge du Roussillon and identified constituents such as camphene,  $\gamma$ -terpinene, hexanol, benzaldehyde,  $\gamma$ -butyrolactone, and nerol for the first time in apricot.
- Later studies on same variety led to the identification of samascone,  $\beta$ -ionone, dihydroactinidiolide, rose oxide and nerol oxide (Rodriguez *et al.*, 1981).
- More than 100 different aroma compounds are present in intact apricot fruit (Takeoka *et al.*, 1990).
- The apricot aroma was supposed to depend on several constituents such as lactones, terpene alcohols and benzaldehyde (Guichard and Souty, 1988).
- The most abundant constituent were C6 lipid degradation products, lactones, aldehydes, terpene alcohols and ketones (Rodriguez, *et al.*, 1980; Rodriguez *et al.*, 1981; Fan *et al.*, 2000; Botondi *et al.*, 2003; Solis-Solis *et al.*, 2007).
- Sharaf (Sharaf *et al.*, 1989) identified 31 components in over ripe apricots of Zibda variety. Other aroma compounds like ethyl acetate, hexyl acetate, limonene, 6-methyl-5-hepten-2-one, menthone, E-hexen-2-al,  $\beta$ -ionone and  $\gamma$ -decalactone are also identified (Solis-Solis *et al.*, 2007).

Recent work on apricot flavor have focused on refining extraction techniques for volatile compounds (Chen *et al.*, 2006; Guillot *et al.*, 2006; Solís-Solís *et al.*, 2007) as well as changes in volatile composition during fruit development (Gomez and Ledbetter, 1997) and storage (Defilippi *et al.*, 2009). The aromatic quality of the apricot increases during its ripening process and is associated with ethylene production (Song and Bangerth, 1996; Singh *et al.*, 2003). Certain aromatic compounds can also be utilized as molecular tracers to discriminate apricot varieties (Rodriguez *et al.*, 1980). Despite the number of studies characterizing aromatic changes during fruit ripening no work is done to observe the association of aroma composition and ripening season, which might contribute to improve fruit flavor in late varieties which is examined in more detail in chapter 5.

Apricot is one of the Tasmanian favourite summer fruits. Its main qualities according to consumers are its convenience and its flavor. But the sensory quality of apricots is irregular and often consumers are disappointed. This leads to very low consumption frequencies, especially when compared with other summer fruit, such as peaches. Producers and retailers need tools to control apricot quality to improve this situation. The present study of flavor compounds will help to evaluate the effect on boron and ReTain® on aromatic potential of three varieties of Tasmanian apricots.

### **A. Extraction Methods**

Earlier studies employed classical flavor procedures of steam distillation and solvent distillation (MacLeod and Pieris, 1984; MacLeod and Snyder, 1985) static headspace (HS) extraction (Vitenberg and Ioffe, 1989; Kolb, 1999), liquid liquid extraction (Yong *et al.*, 1987), simultaneous distillation and extraction (Reglero *et al.*, 1991), solvent extraction and solvent microextraction (Lin *et al.*, 2006; Sarafraz-Yazdi and Es'haghi, 2006), supercritical fluid extraction (SFE) (Lao *et al.*, 1999; Matthew and Clement, 2006) and purge and trap headspace sampling (Forney *et al.*, 1995).

### **B. Selection of the Extraction technique**

Methods based on the use of solvents have several drawbacks such as possibility of sample contamination, the loss of analytes during the concentration process and environmental problems related to the use of large amount of organic solvent (López-Sebastián *et al.*, 1998). The purge and trap method for headspace analysis is unsuitable for liquids containing high level of soluble solids as these may be carried over into the trapping system (Baldwin *et al.*, 1997).

Chances of cross contamination increases and the use of high flow rates can sometimes be incompatible with on-line operation, mainly when GC-MS is used with narrow bore columns. The analysis of flavors is very demanding, because of the wide range of odour thresholds of the individual compounds – because man is much more sensitive to some than others (Blank, 1997).

One-dimensional capillary gas chromatography (1DGC) is routinely used to separate the volatile constituents of food samples. The complex nature of these samples requires long GC run times to obtain the maximum separation power, and even then coelution frequently occurs and is a major challenge for complete qualitative analysis, even with the use of definitive confirmation technologies such as mass spectrometry (MS).

As mentioned above, some aroma-active compounds, or key flavors, are usually present in ultra-trace amounts and are not usually the major volatile constituents of the food. When using GC with olfactometric detection the human nose can often detect a distinctive smell where the chromatogram produces a flat baseline (Blank, 1997). Even more frustrating, a substance that does elute at the proper retention time is not necessarily responsible for that smell – the aroma-active compound(s) might well be hidden by artefacts present at higher concentrations.

Obviously, there is a distinct need for a greater separation power; this can be achieved by using a multidimensional GC (MDGC) producer ( Catalfamo *et al.*, 1998; 1999). Unfortunately, because of the considerable increase in analysis time, conventional MDGC heart-cutting methods are limited to the analysis of only a few discrete target regions of a chromatogram. In addition, they require sophisticated instrumentation and experienced analysts. HS sampling for GC analysis has many advantages, the most important of which is elimination of many of the interferences in the sample matrix. HS-GC analysis of trace volatile compounds in samples is often difficult, because of their very low concentrations.

In recent years solid-phase micro-extraction (SPME) has become an elegant option for sample preparation in aroma analysis, enabling rapid sampling at low cost with ease of operation and adequate sensitivity (Arthur and Pawliszyn, 1990; Yang *et al.*, 1994). Various methods were also compared in the literature to determine the most effective method and finally SPME was found to be the economical and reliable way of concentrating, storing and transporting samples of volatile and semi volatile compounds of the fruit.

### C. Solid Phase Microextraction (SPME)

Solid phase microextraction (SPME) is a new method for the extraction of organic compounds from different matrices e.g. air and water and an alternative to traditional extraction procedures such as purge and trap procedures or solid phase extraction. First described by Pawliszyn and coworkers (Arthur and Pawliszyn, 1990; Potter *et al.*, 1992; Arthur *et al.*, 1992), this technique is based on chemically modified fused silica fibers fixed inside a syringe.

As the coating headspace partition co-efficients of the most volatile organic compounds are relatively small, the extraction yields and thus the limits of detection of such compounds are not satisfactory. To improve the enrichment of such compounds Mangano and Cenciarni (1995) developed a fused silica fiber coated with graphitized carbon black Carbograph I (Alltech) with increased thermal stability and reported extraction and calibration curves of volatile organic compounds in gaseous and aqueous samples.

### D. Advantages of SPME

SPME is a rapid, simple and inexpensive analytical technique for extracting and preconcentrating fruit flavor. It saves on separation time, solvent purchase and disposal costs and thus improves the detection limits. SPME have been used routinely with GC and GC-MS ( Lord *et al.*, 2000). SPME has been extensively used for flavor and fragrances. These samples commonly have components that may undergo processes of thermal decomposition, oxidation, photolysis etc., and the possibility of such undesirable processes during SPME is favorably reduced due to the simplicity of the sample manipulation ( Valente *et al.*, 2000).

Recently the use of the SPME has been increasing for the extraction of organic compounds from several matrices such as volatile compounds of tomato juice (Selvaggini *et al.*, 2000), sulphur compounds in beer (Hill and Smith, 2000), freshness of fish (Hayman *et al.*, 2001), hydrocarbons in blood ( Hara *et al.*, 2000), free volatile fatty acids in waste waters (Bayona *et al.*, 2000), pesticide residues in fruits and fruit juices (Simplício and Vilas Boas, 1999), water samples (Peñalver *et al.*, 1998; Tavazzi *et al.*, 1999) and serum (Watanabe *et al.*, 1999).

### **2.3.8 Nutritional Value**

Nutritional value is an extremely important quality factor that is impossible to see, taste, or feel. This quality factor is becoming increasingly valued by consumers, scientists and the medical profession as phytonutrients, functional foods and antioxidants become more appreciated. The constituents obtained by the human body from fruits include water, carbohydrates, fats, proteins, fiber, minerals, organic acids, pigments, vitamins and antioxidants among others.

Fruits are consumed at all times due to their convenient size and they are excellent between meal snacks. Most of them are low in calories and fat with absence of cholesterol (Crisosto *et al.*, 2004b). They are rich in carbohydrates and fibre, Vitamin C, carotene and Vitamin B6. Fruits are relative low in sodium and high in potassium.

Ascorbic acid in fruits and vegetables enhances the bioavailability of iron in the diet (Hurrell, 1997). As a result, they have a unique role in a healthy diet. Whole grains, fruits and vegetables are considered very good sources of fiber (Anderson *et al.*, 2007). Fiber contents of fruits and vegetables are usually in the range of 1% to 3%. Diets rich in fruits and vegetables have been shown to reduce the incidence of cardiovascular disease and some chronic and degenerative diseases associated with oxidative damage (Ames *et al.*, 2003). The incorporation of fruits in the diet may also help in elimination of certain toxins due to the presence of the antioxidants. Antioxidants are present in all plant organs and include ascorbic acid, carotenoids, vitamin E and phenolic compounds (Larson, 1998).

Apricots are rich in minerals such as potassium and vitamins A and vitamin C. They are very low in cholesterol, sodium and saturated fat, with a high amount of dietary fibre. The apricot fruit is an important source of provitamin A carotenoids. 250 gm of fresh or 30 g dried fruit provides 100% of the recommended daily allowance (Bolin and Stafford, 1974). The major carotenoid compound in apricots is  $\beta$ -carotene, constituting 60-70% of the total carotenoids level. Vitamin A is necessary for epithelia tissues covering our bodies and organs, eye health, bone and teeth development and working of endocrine glands. Moreover, Vitamin A plays important role in reproduction and growing function of our bodies and in increasing body resistance against infections (Ahmed *et al.*, 2009).

Apricot kernels contain Laetrile, considered by some to have anti-cancer effects. Critics of laetrile warn the public that eating apricot kernels is dangerous.

## 2.4 Factors influencing fruit quality

Quality cannot be improved after harvesting, therefore, it is important to harvest fruits and vegetables at the proper stage, size and at optimal quality (Bachmann and Earles, 2000). While post-harvest horticulturists have generally focussed on harvest maturity (Kader and Mitchell, 1989a) and temperature management (Mitchell, 1987; 1989) as their starting point, many earlier decisions will profoundly influence the post-harvest performance of the fruit.

Some of these decisions even predate orchard planting, such as variety, local climate, and production system. Others depend on orchard management such as water supply, mineral nutrition, canopy management and fruit load. Conditions in the field before harvest influence quality and shelf life after harvest. The handling practices during harvesting, pre-cooling, grading, packing, storage and transportation can all affect quality.

Apricot fruits are highly perishable. When apricot is harvested in an optimal quality stage, fruits have a very limited market life; because of this fruits are picked mainly in an early pre-climacteric stage, before initiation of ripening, although this creates further difficulties in trying to achieve very good quality. Therefore, techniques to improve storage life of fresh apricots without loss of important quality attribute need to be explored.

### 2.4.1 Pre-harvest factors

Pre-harvest factors such as genetic potential, climatic conditions and cultural practices all influence quality at harvest, as well as shipping and storage stability. Pre-harvest stress conditions can affect the flavor, microbial quality and composition of fruit. Post-harvest life, however, can be maintained and extended by optimized handling and reducing damage through the application of correct post-harvesting techniques (Pineiro and Diaz, 2007). The aim of postharvest handling of locally grown produce is to deliver quality produce to the consumer.

#### 2.4.1.1 Genetic

Recently there has been a significant amount of work reported on the modifications of genetic makeup to improve the post-harvest performance of fruits (Garratt *et al.*, 2002; Valpuesta, 2002; Wehling, 2000). Transgenic fruits have been produced that have reduced browning and softening tendencies, increased shelf life (Garratt *et al.*, 2002) and uniformity of flavor and color. Garratt *et al.* have discussed development of transgenic fruits such as apple with reduction in the incidence of bitter pit, banana with delayed ripening and increased bruising resistance, melon with altered ripening and strawberry with delayed softening and ripening.

A fundamental problem with apricot fruit is the choice of quality rootstock. Generally interstocks are used to overcome incompatibility between the stock and the scion. Interstocks also affect precocity of bearing and fruit quality and reduction of scion growth (Parry and Rogers, 1972). Plant growth and nutritional status of apricot trees is affected by the genetic material used as well as rootstock/scion combination (Stoilov *et al.*, 1979).

Apricot is one of the most popular temperate fruit tree species having a large genetic variability with a strong interaction among cultivars and their area of cultivation (Bailey and Hough, 1985). Depending on the classification system, the number of apricot species ranges from 3 to 12. Six distinct species are usually recognized: *P. brigantina* Vill., *P. holosericeae* Batal, *P. armeniaca* L., *P. mandshurica* (Maxim), *P. sibirica* L., Japanese apricot *P. mume* (Sieb.) Sieb. & Succ. Vavilov placed apricot in three centers of origin: the Chinese center (Central and Western China), the Central Asiatic center (Afghanistan, northwest India and Pakistan, Kashmir, Tajikistan, Uzbekistan, Xinjing province in China and western Tien-Shan), and the Near-Eastern center (interior of Asia Minor). Kostina further divided the cultivated apricot according to their adaptability into four major ecogeographical groups : (1) the Central Asian group, (2) the Iran-Caucasian group, (3) the European group, and (4) the Dzhungar-Zailij group. Many local cultivars are grown in the different areas and producing countries; however, these cultivars lack important traits that needed by modern production and marketing systems.

Some of the most significant evolutionary trends in apricot domestication are related to enhancement of fruit quality, selection of non bitter seeds cultivar, frost resistant cultivars and a gradual change in biology of sexual propagation from self incompatible to self fertile.

#### **2.4.1.2 Climatic**

The growing region and environmental conditions specific to each region, such as temperature, humidity, light, wind, soil, texture, elevation and rainfall significantly influence the quality of fruits (Kader and Barrett, 2003; Salunkhe *et al.*, 1991; Schreiner *et al.*, 2000). The duration, intensity and quality of light during cultivation affect the quality at harvest. Lack of light may prevent adequate fruit color development through molecular interactions with the fruit genome (Tako *et al.*, 2006). Stone fruits as a group are very responsive to high temperature exposure, such as can be induced by delays between harvests and cooling. Problems can include high temperature injury, sunburn, rapid softening, excess water loss and shrivelling, and greater sensitivity to other disorders. The effective pollination period (EPP) of apricots in the warm climatic conditions of the south Mediterranean is extremely short, which was largely due to a short stigma receptivity period (Eghe and Burgos, 1992).



### 2.4.1.3 Cultural practices

Soil type, soil nutrient availability, fertilization and water supply, pruning, thinning, pest control or chemical & growth regulator sprays and density of planting influence the quality of plant produce (Crisosto *et al.*, 1997; Pantastico, 1975). Fertilizer addition affects the mineral contents of fruits, while other cultural practices such as pruning and thinning may influence nutritional composition by changing fruit crop load and size (Kader and Barrett, 2003). Pesticides residues may give rise to flavor taints in fresh products and excessive use of pesticides may even produce harmful metabolites and toxicity (Salunkhe and Desai, 1984). Weather conditions influence the fruiting process because pollination, stigma receptivity, ovule fertility, ovule longevity and fruit set in apricots are directly related (Ruiz and Egea, 2008; Egea and Burgos, 1992).

Design of harvest systems is one of the important elements which have effect on mechanical harvesting. Mechanical properties, affects of land condition, shaking frequency, shaking amplitude, shaking time, velocity of air etc. of the harvesting systems are some of these parameters. Some researchers have proposed optimum values for shaking frequency and shaking amplitude, which must be applied in apricot harvesting (Sansavini *et al.*, 1983; Gezer, 1997).

Mechanical harvesting (limb shakers and trunk shakers) has recently been applied to fresh apricots in Turkey where there is very short period of harvesting and labour is in short supply. The basic principle of limb shaking is based on the transmission of vibratory forces to the limb (Erdogan *et al.*, 2003).

Hand harvesting of apricots is the most time-consuming task in apricot cultivation under Spanish conditions, accounting for more than 60% of the total labour time. As a way to reduce the of this operation, four mechanical harvesting systems have been tested: a hand-carried canvas structure, to catch the fruits, and a hand-held petrol vibrator; a tractor lift-mounted trunk shaker with an inverted umbrella; a tractor-trailed trunk shaker with an inverted umbrella; and a continuous-travel, shake-and-catch harvesting machine in Spain. The harvested apricots are used in processing industry.

A major problem associated with mechanical harvesting is fruit damage, which can affect the fruit quality. Hence it is usually not used for high quality fresh fruit production. However, fresh apricots are not harvested mechanically in Tasmania.

### 2.4.2 Harvesting factors

Maturity at harvest is the most important quality criteria as it directly affects composition, quality, losses and storage potential of plant. The optimum harvest maturity is vital to achieve maximum post-harvest life of fresh produce (Kader and Rolle, 2004).

Any maturity index should clearly separate fruit based on physiological maturity, and any legal standard should be independent of growing conditions or location (Crisosto, 1992; Kader and Mitchell, 1989b).

Fruit harvested at too high a maturity will be incapable of withstanding the rigors of post-harvest handling & distribution and may have increased susceptibility to invasion by fruit rotting organisms (Mitchell *et al.*, 1991). These fruits have short post-harvest life and may develop undesirable off flavors and mealy texture. The optimum maturity of fruit for fresh consumption and processing is determined by the purpose for which it will be used. Several indices as discussed in 2.2 are used to evaluate the maturity for harvest. Each method has its own limitations and advantages and accurate assessment can only be done using a combination of indices (Kitinoja and Kader, 1995; Rickard *et al.*, 1978).

Harvested fruits should not be placed directly on the soil or be exposed to sunlight, heat and rain. Exposure to sun can lead to a high internal temperature, which is detrimental to the quality (Rickard *et al.*, 1978). A simple shade or grass coverage can provide protection for the harvested products (Salunkhe and Desai, 1984). Picking during early morning and late evening is preferable and harvesting after rains should be avoided. Mechanical damage during harvesting and associated handling operations can result in defects on the produce and permit invasion by disease causing microorganisms (McGlasson *et al.*, 1998).

Recent apricot orchards have been designed for densities of 600-1000 trees/ha (Sansavini and Giannerini, 1991; Marinov and Babayashev, 2001). According to Bassi (1999) apricot trees, trained as vase and spindle shapes might be planted at densities of 500 to 1000-1300 per hectare. The increase of planting density leads to growth restriction and yield increase but at the same time irregular fruit ripening, increased diseases and poor fruit quality can occur.

### **2.4.3 Post-harvest factors**

#### **2.4.3.1 Humidity**

Fresh fruits contain sizable amounts of water, for example watermelon may contain 95% of its fresh weight as water. The loss of water manifests itself as symptoms of shrivelling, wilting and loss of crispiness. The reduction of saleable weight and loss of sensory characteristics lower the marketing value. Weight loss by even 5% makes certain produces unsalable (Salunkhe and Desai, 1984).

Some products e.g. chestnuts are soaked in water after harvest to ensure full hydration and may increase harvested weight and storability (Jestin and Poggi, 1984).

### **2.4.3.2 Temperature**

Temperature management is an important tool in post-harvest handling of plant produce to control both physiological and pathological deterioration. Stone fruits can face problems such high temperature injury, rapid softening, excess water loss and shrivelling and greater sensitivity to other disorders. Thus protection from heating after harvest and rapid movement to cooling is important. This is especially important with high maturity fruit, to avoid excessive flesh softening, but can also help to reduce the detrimental effects of internal breakdown (Crisosto *et al.*, 1995).

Post-harvest changes of apricots are delayed when fruits are cooled immediately after harvest and held at low temperatures. Low temperatures delay ethylene production and prevent softening. Forced air cooling is adapted to a wide range of commodities including apricots (Mitchell & Waser, 1992).

### **2.4.3.3 Atmospheric gas composition**

Atmospheric gas composition such as levels of oxygen, carbon dioxide and ethylene influence microbial decay and physiological processes such as respiration. Carbon dioxide combined with oxygen affects fruit shelf life mainly by delaying respiration and ripening as well as by retarding the growth of most aerobic spoilage microorganisms. However, under certain conditions, the growth of some anaerobic psychotrophic pathogens may occur or even be stimulated (Soliva-Fortuny and Martin-Belloso, 2003). The beneficial or harmful effects of varying gas composition depend, however, upon commodity, cultivar, physiological age, oxygen and carbon dioxide levels used temperature and duration of storage (Kader, 1992; Wills *et al.*, 1998).

### **2.4.3.4 Light**

Light post-harvest, may influence the quality of fruits by controlling the synthesis/degradation of pigments responsible for color (chlorophyll and carotenoids), flavor by catalysing oxidation of lipids, sprouting, reducing nutritive value by degrading vitamins such as ascorbic acid and riboflavin, and production of toxins (Mishra and Gamage, 2007).

The duration, intensity and quality of light during cultivation affect the quality at harvest. In tomatoes, leaf shading of fruit is known to result in a deeper red color during the ripening and when grown in full sun light contains more sugar and dry matter (Winsor, 1979). Exposure to the sun tends to make citrus fruit lighter in weight with thinner rind, low amount of juice and acids and high solids content compared to those that were shaded and those inside canopy. The differences in day length and light quality affect the product physiology (Wallace *et al.*, 1969).

The time to peak ethylene production was also delayed by 2 to 5 days in avocado in exposed sunlight compared to fruits kept in shade. To the exposed side of the sun, avocado was generally firmer than the unexposed side, and the average firmness was greater than that of shade fruit (Woolf *et al.*, 1999)

#### **2.4.3.5 Mechanical injury**

Mechanical injuries expose internal tissue to contamination, increase respiration rate, promote chemical and enzymatic reactions (i.e. browning), allow the spread of decay micro organisms, and induce an overall quality decline. Vibration or abrasion bruising can result from fruit movement or rubbing during handling or transportation (Mitchell and Kader, 1989b). Incidence of injuries can be reduced by avoiding opportunities for fruit to abrade during handling and by packing the fruit so they will be immobilized during transport.

Recent studies of black staining of peaches and nectarines (Cheng and Crisosto, 1994; Crisosto *et al.*, 1993) have shown that discoloration can be the result of metal ion contamination of wound areas especially by Fe, Al and Cu ions. Even foliar nutrient sprays and certain orchard fungicides can cause problems if applied too close to harvest. Brushing and waxing of these fruits may increase susceptibility to the disorder.

One of the major problems of mechanical harvesting of apricot is the higher level of bruises. It is found that morphological structure of tree, pruning method, level of maturity, altitude and frequency applied during harvesting, dynamic properties of fruits, falling height and ground conditions have an effect on mechanical bruising. It is suggested that by using V and T type pruning fruit bruising can be decreased by 10% (Tuncer and Ozguven, 1989). Using a catching platform, bruising is decreased by 78% (Gezer, 1997).

Apricot is a typical fruit in which the mechanical injury (bruising) shows up only when the fruit becomes ripe (De Martino *et al.*, 2002). Since apricots are picked at an early stage of ripening, any mechanical damage becomes evident when the product reaches retail shops and consumers. Furthermore, the presence of bruises hastens the ripening process, which strongly reduces the shelf-life of the product. Identification of hidden damage at an early stage, during the sorting process in the packinghouse, will allow for the reduction of apricots rejection at the retail level (Natale *et al.*, 2006). Hand- harvest will most likely remain the method of choice for fresh-market apricots, because of excessive fruit injury, increased susceptibility to decay and the greater need for selecting fruits at optimum maturity when mechanical harvesting is used (Kader, 1983).

## 2.5 Mineral nutrition

The quantity and biological quality of fruit tree yields depend on both irrigation and fertilization (Rzekanowski and Rolbiecki, 1996; Castel, 2006). Production of large quantities of fruit is as important as to maintain high quality of fruit (Morgas and Szymczak, 2007). Concentrations of mineral components in orchard plants are very important for both agro technology reasons to maintain good fruit quality parameters such as e.g. fruit size, color, and firmness (Chaverria *et al.*, 2005) and human nutrition. Plants require a balanced mineral intake for proper development, so a deficiency in any essential mineral will lead to poor development of the tree as a whole. Site and soil conditions affect apricot tree growth, significantly, with a strong soil site interaction (Brun *et al.*, 1991).

Nutrition is a complex process involving 16 essential nutrients as well as many other chemical elements that are either beneficial or harmful to plant metabolism. The sixteen chemical elements are divided into two main groups: non mineral and mineral. The non-mineral nutrients are hydrogen (H), oxygen (O) and carbon, which are found in air and water and made available through water uptake and photosynthesis. Thirteen mineral nutrients which come from soil are dissolved in water and absorbed through plant's roots. Generally the availability of all these nutrients is not sufficient in soil for a plant to grow healthily. Thus growers apply external fertilizers to provide nutrients to the soil. The mineral nutrients are divided into two groups: macronutrients and micronutrients.

### 2.5.1 Macronutrients

Elements required by plants in relatively large amounts are called macronutrients. Macronutrients can be broken into two major groups, primary and secondary nutrients. The **primary nutrients** are comprised of nitrogen (N), phosphorus (P) and potassium (K). These major nutrients are usually the first to become lacking from the soil because plants use large amounts for their growth and survival. The **secondary nutrients** are calcium (Ca), Magnesium (Mg) and sulphur (S), which are usually present in adequate quantities in soil, so their fertilization is often not mandatory. Also large amounts of calcium and magnesium are unavoidably added when lime is applied to acidic soils to amend the pH of the soil and improve the availability of other nutrients.

The response of trees such as apricot, to a particular nutrient status may vary with cultivar and exogenous factors such as soil concentrations and forms, cultural practices, substrate type and conditions and environmental conditions. The provision of nutrients to the plant in quantities that are optimal for their subsequent utilization is a primary aim of crop fertilizer programmes. The fruit yield and quality are adversely affected by any deviation from this optimum quantity (Passam *et al.*, 2007).

### 2.5.1.1 Nitrogen (N)

Nitrogen is the only nutrient that can be supplied to plants in both anionic ( $\text{NO}_3^-$ ) and cationic ( $\text{NH}_4^+$ ) forms (Forde and Clarkson, 1999). Nitrogen is an essential component of all proteins as well as various structural, metabolic and genetic molecules. Nitrogen deficiency most often results in stunted growth, slow growth, and chlorosis. Nitrogen deficient plants will also often exhibit a purple appearance on the stems, petioles and underside of leaves from an accumulation of anthocyanin pigments (Huner and Hopkins, 2004). Application of N has been reported to affect other aspects of fruit quality including a reduction in acidity and increase in the pH of fresh apricots (El-Sayed and Luh, 1967; Dimitrovski and Cevetkovic, 1981). In apricots total soluble solids (Bussi and Amiot, 1998) and firmness (El-Sayed and Luh, 1967) are not affected by Nitrogen.

A relationship between N level and fresh fruit and the darkening of the dried apricots during storage has been established in Moorpark apricot orchards (Rettke *et al.*, 2001). N application to apricots trees has effects on tree growth, yield and fruit characteristics (Dimitrovski and Cevetkovic, 1981; Bussi *et al.*, 2003). Fruit maturation is delayed by over fertilization (Albrigo *et al.*, 1966). High nitrogen increases the variability of maturity among fruit on a tree and even among different parts of the fruit (Claypool, 1975). For example in apricots the styler end may be ripe while the stem end is still green. This effect of delaying maturity makes it very difficult to evaluate other fruit quality parameters, since the fruit have different picking times and might have different physiological maturity.

### 2.5.1.2 Phosphorous (P)

Phosphorus is important in plant bioenergetics. As a component of ATP, phosphorus is needed for the conversion of light energy to chemical energy (ATP) during photosynthesis. Phosphorus can also be used to modify the activity of various enzymes by phosphorylation, and can be used for cell signalling. Since ATP can be used for the biosynthesis of many plant biomolecules, phosphorus is important for plant growth and flower/seed formation. Phosphate esters make up DNA, RNA, and phospholipids. Most commonly in the form of polyprotic phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in soil, but it is taken up most readily in the form of  $\text{H}_2\text{PO}_4$ . Phosphorus is limited in most soils because it is released very slowly from insoluble phosphates. Under most environmental conditions it is the limiting element because of its small concentration in soil and high demand by plants and microorganisms. Plants can increase phosphorus uptake by a mutualism with mycorrhiza (Huner and Hopkins, 2004).

A Phosphorus deficiency in plants is characterized by an intense green coloration in leaves. High phosphorus deficiencies leads to leaf distortion and a red to purple color change in leaves followed by marginal the necrosis (Costello,2003). Occasionally the leaves may appear purple from an accumulation of anthocyanin. Because phosphorus is a mobile

nutrient, older leaves will show the first signs of deficiency. High phosphorus content fertilizers, such as bone meal, are useful to apply to perennials to help with successful root formation. Increased N and P soil application resulted in increase in total fruit yield in apricots (Asma *et al.*, 2007).

### **2.5.1.3 Potassium (K)**

Potassium is the major solute for osmotic regulations in plants. It is important as an activator of several enzymes. Potassium regulates the opening and closing of the stomata by a potassium ion pump. Since stomata are important in water regulation, potassium reduces water loss from the leaves and increases drought tolerance. Potassium deficiency may cause necrosis.  $K^+$  is highly mobile and can aid in balancing the anion charges within the plant. It also has high solubility in water and leaches out of soils that are rocky or sandy and this can result in potassium deficiency. It serves as an activator of enzymes used in photosynthesis and respiration (Huner and Hopkins, 2004). Potassium is used to build cellulose and aids in photosynthesis by the formation of chlorophyll precursor.

Both high and low levels of Potassium have been associated with abnormal metabolism. High levels of potassium have been associated with the development of bitter pit in apple so that both high potassium and low calcium levels are correlated with pit development. Bitter pits result when there is competition between leaves and fruits for calcium. Calcium uptake can be influenced by excessive amounts of K and Mg, which directly competes with calcium within the fruit cells. K, Mg and Ca are chemically similar as all of them are positively charged ions. Due to their chemistry K and Mg are often taken up in preference to calcium. Low potassium is associated with changes in the ripening of tomato and delays the development of a full red color by inhibiting lycopene biosynthesis.

Potassium deficiencies are more problematic to prunes than in other stone fruits. As potassium is concentrated in the upper 6 to 8 inches of the soil, deficiencies are more likely to occur where topsoil has been removed or levelled off. Potassium deficiency may result in higher risk of pathogens, wilting, chlorosis, brown spotting, and higher chances of damage from frost and heat. Affected leaves may prematurely with reduction of fruit size and color development. Potassium deficiency predisposes prunes and European plums to Cytospora canker (Strand, 1999).

Potassium is absorbed by apricot trees in significant quantities. One of the desired characteristics in dried apricot cultivars is high TSS content in the fruit. Potassium application had more beneficial effects on TSS content of apricot fruits than N and P applications (Bussi and Amiot, 1998).



#### 2.5.1.4 Calcium (Ca)

Calcium has been associated with more post-harvest deficiency disorders than other mineral. Calcium has been found to be relocated in apples during storage. Calcium is immobile in plants. It is not redistributed from older to younger leaves or from leaves to fruits or seeds. Calcium uptake follows the water uptake and distribution in the plant. Even the foliar application of calcium is not sufficient to provide enough calcium to fruits or vegetables. Hence, soil application is also done along with foliar application. Calcium will not translocate once it is incorporated into the plant cells. Therefore it is critical to supply calcium when new cells are forming. Calcium has been shown to affect the activity of many enzyme systems and metabolic sequences in plant tissues. Calcium is needed for the activity of exo PG, kinases and a range of other enzymes. The ability of calcium to regulate these various systems has led to speculation that calcium may have a role in the initiation of the normal fruit ripening process. It is also possible that calcium prevents or delays the appearance of some physiological disorders by maintaining normal metabolism (McGlasson *et al.*, 1998).

Calcium as a constituent of the cell wall plays an important role in forming cross-bridges which influences cell wall strength and is regarded as the last barrier before cell wall separation (Fry, 2004). Exogenously applied calcium stabilizes the cell wall protection against the degrading enzymes (White and Broadley, 2003). The efficiency of exogenously applied calcium varies according to calcium fertilization studies on apricots (Mohsen, 2011), peach (Lanauskas and Kvikliene, 2006; Manganaris *et al.*, 2005) and apple (Peryea and Neilsen, 2006).

Calcium was shown to accumulate mainly in transpiring organs in a process affected by various environmental conditions at both the canopy and root level, and is considered to be coupled to water movement driven by transpiration although controversies still arise in that relation (Atkinson *et al.*, 1992). Furthermore, as Ca moves mainly in xylem, a conduit under negative pressure, any attempts to sample it en-route will cause cessation of flow. Pre-harvest calcium sprays are one of the most important practices of the new strategies applied in Integrated Fruit Production systems for apricots. They improve fruit characteristics and minimizing fungicide sprays towards the end of the harvest period, since they improve fruit resistance to brown rot (Conway *et al.*, 1992).

Foliar sprays of B and Ca are most commonly used to correct drought stress induced physiological and biochemical responses in plants at both cellular and molecular levels (Shinozaki *et al.*, 2003; Bartels and Sunkar, 2005). The concentration of Ca and B in strawberry leaves and fruits increased with its application, confirming that when these



nutrients are applied through foliar means they are readily available to plants and then translocated to different plant parts (Rajbir *et al.*, 2007).

In fruits, calcium (Ca) deficiency causes various physiological disorders and shortens post-harvest storability (Wills *et al.*, 1998). Calcium and boron are the nutrients that have little mobility in plants, being limited almost exclusively to passive transport in the xylemic flow. Therefore, the synergy existing between the two elements is well documented. Because of this, the boron increases the assimilation and mobility of the calcium in the plant increasing the transport of calcium from the roots to the apical meristems. Calcium and Boron have similar and significant functions (Faust, 1989; Ferguson and Drobak, 1988; and Huber, 1983). Calcium is necessary for the fruit during first phases (young fruit) of growth. It is initially supplied from the Ca stored in the plant and later translocated through xylem flow with the transpiration stream. The amount of calcium a fruit receives may vary significantly due to the competition between leaves and fruits (Hanger, 1979). In rapid transpiration conditions, Ca deficiency occurs (Marschner, 1995; Swietlik and Faust, 1984). This might reduce post-harvest durability in apples (Ferguson and Watkins, 1989).

Double calcium sprays had the most pronounced effect on apricot fruit quality at harvest. Sprays were applied after cold storage and after 5 days of shelf life while spraying at 15 days before anticipated maturity followed as the next most successful strategy (Mohsen, 2011). Calcium sprays reduced fruit decay, weight loss and reducing the rate of fruit softening in apple (Saure, 2005; Hernandez-Fuentes, 2003). Calcium is an important element for cherry fruit quality as it reduces the water absorption and therefore avoids cracking. These enhancements might be due to calcium effects on the cell wall as previously mentioned by Blevins and Lukaszewski (1998).

#### **2.5.1.5 Sulphur (S)**

Sulphur is a structural component of some amino acids and vitamins, and is essential in the manufacturing of chloroplasts (Abdel-Ghany *et al.*, 2005). Sulphur is also found in the Iron Sulphur complexes of the electron transport chains in photosynthesis. It is immobile and deficiency therefore affects younger tissues first. Symptoms of deficiency include yellowing of leaves and stunted growth.

#### **2.5.1.6 Magnesium (Mg)**

Magnesium is an important part of chlorophyll, a critical plant pigment important in photosynthesis. It is important in the production of ATP through its role as an enzyme cofactor. Magnesium deficiency can result in interveinal chlorosis.

### **2.5.1.7 Silicon (Si)**

In plants, silicon strengthens cell walls, improving plant strength, health, and productivity. Other benefits of silicon to plants include improved drought and frost resistance, decreased lodging potential and boosting the plant's natural pest and disease fighting systems (Prakash, 2007). Silicon has also been shown to improve plant vigour and physiology by improving root mass and density, and increasing above ground plant biomass and crop yields. Although not considered an essential element for plant growth and development (except for specific plant species - sugarcane and members of the horsetail family), silicon is considered a beneficial element in many countries throughout the world due to its many benefits to numerous plant species when under abiotic or biotic stresses (Jian and Naoki, 2011). Silicon is currently under consideration by the Association of American Plant Food Control Officials (AAPFCO) for elevation to the status of a "plant beneficial substance" (Stephen and Barker, 2009).

### **2.5.2 Micronutrients**

Micronutrients are those elements essential for plant growth which are needed in only very small (micro) quantities. These elements are sometimes called minor elements or trace elements, but use of the term micronutrient is encouraged by the American Society of Agronomy and the Soil Science Society of America. The micronutrients are boron (B), copper (Cu), iron (Fe), chloride (Cl), manganese (Mn), molybdenum (Mo) and zinc (Zn). Recycling organic matter such as grass clippings and tree leaves is an excellent way of providing micronutrients (as well as macronutrients) to growing plants. Table 2.2 lists the basic functions of all essential micro nutrients.

These elements function in the plant mainly as cofactors of enzymatic reactions in plants. Iron for example is a metallic component of cytochromes, the proteins that function in the electron transport chains of chloroplasts and mitochondria. The symptoms of a mineral deficiency depend on the role of the nutrient in the plant and its mobility within the plant. With free movements of the nutrients, the deficiency will first affect the young growing tissues than old tissues. For example a deficiency of iron, which moves freely in the plant, will cause yellowing of young leave before we can see any effect on older leaves (Campbell, 2000).

Mineral nutrition can be optimized if the plant is grown hydroponically on nutrient solution that can be precisely regulated. Hydroponics is currently practiced commercially, but only on a limited scale because it is very expensive way to grow food compared with growing crops on soil.

<b>Micronutrients</b>			
Chlorine	$\text{Cl}^-$	0.010	Activates photosynthetic elements; functions in water balance
Iron	$\text{Fe}^{3+}$ , $\text{Fe}^{2+}$	0.010	Component of cytochromes; may activate some enzymes
Boron	$\text{H}_2\text{BO}_3^-$	0.002	Uncertain; may be involved in carbohydrate transport and nucleic acid synthesis
Manganese	$\text{Mn}^{2+}$	0.0050	Active in formation of amino acids; activates some enzymes
Zinc	$\text{Zn}^{2+}$	0.0020	Active in formation of chlorophyll; activates some enzymes
Copper	$\text{Cu}^+$ , $\text{Cu}^{2+}$	0.0006	Component of many redox and lignin-biosynthetic enzymes
Molybdenum	$\text{MO}_4^-$	0.00001	Essential for nitrogen fixation; cofactor functional in nitrate reduction

**Table 2.2 Role of micronutrients (Source: Campbell, 2000)**

Unlike roots, foliage is not adapted to absorb large amounts of fertilizer (nutrients). However, foliar spraying is able to take advantage of the significant combined 'surface area' of leaves and stems on a plant (Dr. H. B. Tukey, Dept of Horticulture, Michigan State College). Consequently, when foliage is sprayed with a fertilizer formulation that can be easily absorbed, there is a large opportunity for nutrient input.

Sprays are mainly used for supplying nitrogen, iron and zinc. However, potassium and other trace elements can be absorbed through foliage. Radioactive tests show that micro-nutrients, once sprayed, are in the sap stream within one hour (Sheikholeslam and Currier, 1977). This means foliar sprays can be effective for quickly correcting certain nutrient deficiencies. They are also a useful supplement to root feeding when up-take is restricted because roots are diseased, damaged, or simply too small. Specific foliar fertilizer formulations can be used to influence plant characteristics such as fruit set, fruit size and pest and disease resistance. Zinc deficiency symptoms include short internodes, small narrow leaves, and interveinal chlorosis with shoot and branch dieback. In advanced stages of Zn deficiency, small narrow leaves are arranged in whorls or rosettes.

The relationship between the content of elements in soil, their concentrations in plant tissues, and growth is a complex phenomenon. In most cases, mineral contaminants accumulate in the upper layer of the soil where they are integrated in the complex equilibrium system of precipitates, organomineral complexes, and adsorbed and exchangeable forms of free ions in solutions. Only free aquated metal ions are available to plants, and this fraction depends on pH, organic matter content, redox potential, etc. (Demier *et al.*, 1990).

Injections of copper, iron and cobalt have induced symptoms similar to low temperature breakdown and superficial scald in apples (Wills *et al.*, 1984), but this does not necessarily mean they have a role in the development of the natural disorder. Heavy metals, especially copper, act as catalysts for the enzymic systems that lead to enzymic browning, the browning of cut or damaged tissues that are exposed to air. The levels of these metals are important in processed fruit and vegetables, whether they are derived from the produce or from metal impurities that are included during processing.

Boron deficiency in apples leads to a condition known as internal cork. This condition is marked by pitting of the flesh and is often indistinguishable from bitter pit. The differences between the two disorders are that internal cork is prevented by the application of foliar boron sprays and develops only on the tree, while bitter pit responds to calcium treatment and can develop post-harvest.

## **2.6 Selection of pre-harvest foliar sprays of boron and ReTain®**

Previous research has shown that foliar B application to B deficient trees increases Ca mobility as well as Ca concentration of the fruit (Shear and Faust, 1971), hence the partial interchangeability of B and Ca suggested earlier in some situations. The trees of the experimental site, Qew Orchards, Richmond, Tasmania were believed to be deficient in Boron. The aim of this study was to evaluate the influence of pre-harvest foliar sprays of Boron and ReTain® in quality attributes of apricot fruits during their ripening after harvest. Boron is an essential trace element required for optimal growth and development of higher plants and B shortage is believed to be the most widespread of micronutrient deficiencies in plants (Sparr, 1970). Boron deficient plant exhibit a shrunken aspect, with inhibition in root growth, short stems, affected youngest leaves and deformed fruits.

Plant functions requiring B include sugar transport, cell wall synthesis and lignification, cell wall structure development and maintaining respiration which, are all reflected in changes to basic fruit quality (Blevins and Lukaszewski, 1998). Most Boron is located in the cell wall forming complexes with pectic and galacturonic derivatives with a

specific cis-diol configuration. Boron interacts with polyhydroxy polymers (such as pectins) to form borate ester cross links, that stabilize cell wall structure (Loomis and Durst, 1992).

Boron has significant effects in pollen germination and pollen tube growth. The viability of pollen grains also decreases when B is deficient. Production of fruit, nut and seed crops is adversely affected much more than vegetative growth with a low supply of available B in soil. Recent research findings have greatly improved understanding of B uptake and transport processes (Brown and Shelp, 1997; Brown *et al.*, 2002; Takano *et al.*, 2002, 2005, 2006) and roles of boron in cell wall formation (O'Neill *et al.*, 2004), cellular membrane functions (Goldbach *et al.*, 2001) and anti-oxidative defense systems (Cakmak and Romheld, 1997).

The changes in B concentration may lead to a mechanical cascade of signals starting by an altered conformation of membrane bound proteins (Watson, 1991). The interaction between B and low temperature in warm season species has been recently reviewed, particularly in relation to root functions, shoot water use and B uptake and utilization in plants (Huang *et al.*, 2005).

Calcium and Boron sprayed on leaves can be translocated to bark, floral buds and other plant parts. Boron sprayed on the foliage of Italian prune in autumn is translocated from the senescencing leaves to the adjacent flower buds (Hanson *et al.*, 1985). The radioactive B applied to the foliage of sour cherries move to the wood and bark of the trees. B is shown to be mobile in the species that transport significant amounts of sorbitol in their phloem as in the case of *Pyrus*, *Malus* and *Prunus* (Brown & Hu, 1996; Brown & Shelp, 1997).

Boron source, its concentration, the number of sprays, as well as field conditions is all of critical importance while applying it as foliar sprays. Soil conditions are highly variable. Therefore it is necessary to determine the available B supply when apricots are grown. Both soil and plant tissue analysis are strongly recommended to assess the available B status for fruit and nut crops, and also for agronomic or forage crops that are grown for seed production.

A combination of soil applications and foliar sprays, depending on the plant species may be used, when soil or plant analysis indicate a low supply of available B for the crop. However application of boron in soil sometimes causes phyto toxicity as there is a narrow range between B deficiency and toxicity for many fruit crops including strawberry (Gupta, 1979). Application of AVG to apple trees close to harvest affects ethylene mediated processes such as pre-harvest fruit abscission, fruit ripening and storage life (Autio and Bramlage, 1982; Bangerth, 1978; Byers, 1997; Johnsons and Colgan, 2003; Mir *et al.*, 1999; Schupp and Greene, 2004).



The effects of pre-harvest spray of AVG and AVG in combination with ethephon on color development and fruit quality at harvest are investigated in apples (Whale *et al.*, 2007). AVG is an active constituent in ReTain® Plant Growth Regulators which are commercially used in apple orchards in many countries around the world to delay fruit maturation and to manipulate harvest and storage quality.

ReTain® applied to commercial orchards in Australia delayed the ripening of 'Gala' apples by 9-12 days and of 'Pink Lady' apples by 5 days (Phan-Theien *et al.*, 2004). ReTain® plant growth regulator containing 15% w/w AVG, was registered in Australia in October 2001 for use in apples, peaches and nectarines. Application of ReTain® as a pre-harvest spray to apples, peaches, nectarines and other climacteric fruit delays the onset of the ethylene production associated with the climacteric, delaying both the climacteric and the associated ripening phase of fruit development.

Application of ReTain® to "Artic Snow" nectarines 7 days before the first harvest resulted in a delay in fruit maturation of about 3 days. The firmness of the fruit was increased with delayed ripening time leading to financial advantages (Rath and Prentice, 2004). Among a variety of climacteric (peach, plum, nectarine and apricot) and non-climacteric (sweet cherry) stone fruits, only apricots were adversely affected by continuous exposure to exogenous ethylene, during cold storage (Palou *et al.*, 2002a).

Treatment with 100 ppm ethylene for 48 hrs at 20°C accelerated softening of apricots (Brecht *et al.*, 1982). Therefore the commercial adoption of effective methods to protect harvested apricots against the deleterious effects of endogenous or exogenous ethylene should be considered.

Apricot suffers a rapid loss of quality once harvested, both sensory and nutritional, due to its short climacteric ethylene production. The storage strategy used to control ethylene production and respiration is therefore very important in extending the shelf life of apricots. Therefore in this study pre-foliar sprays of ReTain® were used to analyse its effects on quality parameters of harvested apricots. The influence of foliar sprays of ReTain® on three varieties of apricots is described in detail in chapter 4.

Although the symptoms of boron deficiency are rapid and clear, the primary physiological effect of boron remains unknown. Hence the requirement of boron in the physiology of higher plants is topic open to research and discussion (Varner, 1995) because of this boron is the least understood of all the essential nutrients in higher plants. Therefore, pre-harvest foliar sprays of Boron followed by ReTain® were applied on three varieties of apricot to evaluate the effect of B or ReTain® or B and ReTain® on quality parameter of apricots.

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Different quality measurements

The most important traits of fruit quality in apricots are flavor, total soluble solids, titrable acidity and texture, measured as firmness, and appearance (shape, size, color) (Crisosto *et al.*, 1994, 2004; Harker *et al.*, 2003).

##### 3.1.1 Fruit weight

Fruit fresh weight was measured with a digital balance (Bianco *et al.*, 2010).

##### 3.1.2 Appearance

External sensory attributes of fresh fruit, such as shape, size, color and external defects constitute appearance of the apricots. These are intrinsic quality cues of fruit that are evaluated by the consumer before consumption.

###### 3.1.2.1 Size and shape

Size was measured with digital **Vernier Calipers**. The length, breadth and width of fresh fruit and kernels were measured as primary readings. Other physical measurement such as volume and different size ratios were calculated from the primary readings. The vernier caliper is a precision instrument that can be used to measure internal and external distances extremely accurately. The digital vernier calliper contains an LCD digital display on which the reading appears, it requires a small battery as a power source.

###### 3.1.2.2 Color

Visual appraisal and instrumental color analysis are the only two choices for food color evaluation. To pursue trends in consumer preference, visual appraisal is recommended and if a manufacturer is interested in tracking color changes for quality assurance, instrumental color analysis can be done. The visual appearance of fruit is the most important quality factor as it decides its price in the market. The consumer, wholesaler or retailer judges the quality of apricots based on their visual or external appearance. For our experiments visual analysis was performed. There were a large number of fresh apricot samples that needed to be processed for size, shape and firmness. Under these circumstances it was better to perform a color test with the rapid visual analysis as chemical methods were too time consuming and not fully justified in this study.

When selecting visual evaluation, sensory scientist can choose either a consumer panel or a trained descriptive panel. However, the presenters cautioned that consumer panels are less suitable for accurately describing color; rather they are ideal for predicting consumer preference using hedonic scales which are described in detail in Chapter 6.

### **3.1.3 pH**

The pH value of fruits including apricot is a direct function of the free hydrogen ions present in the fruit. Acids present in fruits release these hydrogen ions, which give acid foods their distinct sour flavor. Thus, pH may be defined as a measure of free acidity. Moreover, the taste effects associated with pH may give rise to secondary effects from the level of acidity in the fruit. One such effect is on pectin chemistry in the apricot. In apricots, it has been observed that soluble pectins undergo some depolymerisation and that the average molecular weight is significantly decreased (Fischer and Bennett, 1991). The route to achieve these modifications can be dependent on the starting wall composition as well as the capacity of the fruit to maintain wall synthesis, production of hydrolytic enzymes and pH conditions in the apoplast (O' Donoghue *et al.*, 1997).

To measure pH frozen apricots were bought to room temperature and homogenized at high speed with an Ultra Turrax (IKA® Works Asia Sdn Bhd, Serendah, Malaysia) with a shaft diameter of 10mm (Figure 3.3) for 90 s. The juice was centrifuged at 7000g for 20 mins at 4°C so that heavy cells settled down and juice was drained with the help of muslin cloth. The same sample was used to measure pH and titrable acidity with an Automatic Metrohm Titrator.

### **3.1.4 Fruit firmness**

As apricots mature and ripen they soften by dissolution of the middle lamella of the cell walls. The degree of firmness can be estimated subjectively by finger or thumb pressure, but more precise objective measurements are possible with a pressure tester or penetrometer. In many fruits such as peach, plum, apricot etc. firmness can be used to determine harvest maturity.

The knowledge of the degree of firmness or ripeness of apricot is a factor of considerable commercial importance as it enables importers and distributors to assess the shelf life of the fruit. It helps in analyzing whether the quality of the apricot meets the requirement of supermarkets and other retail outlets in this regard.

Penetrometers measure the pressure necessary to force a plunger of specified size into the pulp of the fruit. Such pressure is measured in kilograms force or pounds. Producers, packers and distributors use the penetrometer to help determine the stage of



ripeness of a fruit and by the retail trade to determine palatability for the consumers. The determination of firmness of a fruit by means of the penetrometer is based on the pressure necessary to push a plunger of specified size into the pulp of the fruit up to a specific depth.

The choice of plunger size and scale range used will depend on the type and variety of the produce being tested and its stages of maturity. Three detachable plungers are available one of 8mm diameter generally suitable for use in testing softer produce (e.g. peaches, nectarines, plums), one of 11 mm (1 cm<sup>2</sup>) diameter generally suitable for use in testing harder fruit (e.g. apples, pears) and a pointed plunger for use in testing avocados. Fruit firmness in our project was measured using a stand mounted pressure tester equipped with 8mm plunger tip. Ideally, the penetrometer should be bench mounted on a fixed, rigid drill stand to ensure that pressure is applied at a steady controlled rate and at a constant angle to the fruit i.e. vertically downwards.

#### **3.1.4.1 Procedure**

1. From two opposite sides of the equatorial area of the fruit a disc of peel (only skin depth) of up to 2 cm<sup>2</sup> was removed with a sharp knife.
2. The penetrometer was zeroed and the plunger head placed against the fleshy portion of apricot in the peeled area of fruit. The fruit was held firmly and rested on a rigid surface such as table top, or the plate at the base of the stand.
3. Uniform downwards pressure was applied until the plunger had penetrated the flesh of the fruit up to the depth mark on the plunger. The plunger was removed and reading was noted.
4. The process was repeated on the opposite side of the same fruit making sure to zero the penetrometer. It was important to conduct all tests as uniformly and carefully as possible in order to allow an accurate comparison of results.
5. The two readings for each individual fruit were averaged and noted as final firmness of the specific sample.

#### **3.1.4.2 Selection of sample**

1. A random of 12 apricot samples of each treatment was selected from several fruits..
2. Selection of apricot fruit was for uniform size to avoid variation in firmness due to size (large fruit are usually softer than smaller fruit).
3. All apricots tested were comparable in temperature since warm fruit are usually softer than cold fruit.

### 3.1.4.3 Proper units for firmness

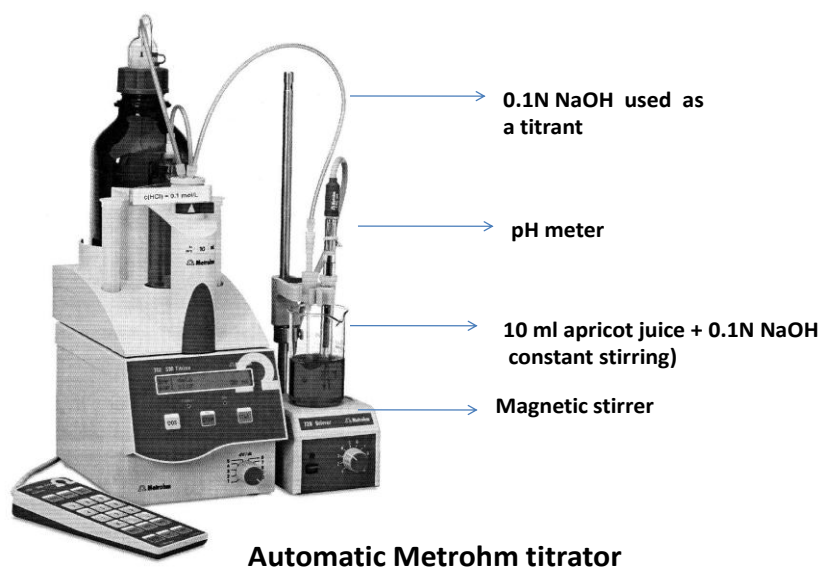
It is inappropriate to use the term “pressure” in association with firmness measurements using the devices described above. While pounds-force or kg-force are preferred in the industry, Newton (N) is the required unit for scientific writing. The conversion factors are as follows:

$$\text{pound-force (lbf)} \times 4.448 = \text{Newton (N)} \quad \text{kilogram-force (kgf)} \times 9.807 = \text{Newton (N)}$$

### 3.1.5 Taste

#### 3.1.5.1 Titrable acidity

The acidity of a juice is due to the content of several organic acids (i.e. citric, malic, fumaric, acetic, ascorbic, galacturonic). The acidity of a fruit juice is relevant to keep the organoleptic nature inalterable and to avoid fermentation processes. These properties make the determination of this parameter of great interest. The usual method for the determination of titrable acidity in fruit juices is the AOAC procedure (Helrich, 1990) based on the titration of a sample with 0.1 N NaOH, using phenolphthalein as indicator or potentiometric detection in the case of heavily colored samples. However for our experiment we used an automatic titrator (702 SM Titrino, Metrohm, Switzerland).



**Figure 3.1 Automatic titrator**

Titration acidity of apricot juices measures the concentration of titration hydrogen ions contained in the apricot juice sample, by neutralization with strong base solution at a fixed pH. This value includes all the substances of an acidic nature in the apricot juice: free hydrogen ions, organic acids, acid salts and cations.

As organic acids are the most acidic component of the fruit juices that reacts with strong bases solutions, the titration acidity (TA) is usually expressed as g/L or g/100mL of the predominant acid contained.

$$TA( \text{g/L} ) = \frac{\text{ml NaOH} \times (\text{NaOH}) \times \text{aid.meq. Factor}^* \times 100}{\text{Juice titrated}}$$

\*the following acid meq. factor may be used for different fruits.

Acid	Acid meq. factor	Commodities
Citric	0.0064	Berries, citrus, fruits, pineapple
Malic	0.0067	Apple, pear, peach, tomato
Tartaric	0.0075	Grape

Titration acidity (TA) of fruit is an important parameter in determining fruit maturity. For determination of TA, 12 frozen apricot samples of each treatment were brought to room temperature. The fruit was homogenized with a commercial homogenizer and titrated with 0.1 N NaOH to pH 8.2 with the automatic titrator. Results were expressed as percent of malic acid, citric acid and tartaric acid.

### Procedure

1. Standardise the pH meter with pH buffer solution 4 and pH buffer solution 7. Set the temperature at 20°C and titration method, which in our case was the standard graph method. Set titration end point at pH 8.2.
2. Fill the bottle with 0.1N NaOH.
3. Rinse the pH electrode with distilled water and gently dry. Discard the rinse water.
4. Add 20 ml of the apricot juice to the beaker with a stirrer and as shown in Figure 3.1.3 arrange it on a magnetic stirrer.
5. Make sure the temperature of the sample is approximately 20°C. The pH electrode should be adequately covered with the apricot juice. It should not touch the bottom or sides of the beaker.
6. Position the burette tip as centrally as possible and switch on the start button. Switch on the magnetic stirrer and set it on appropriate position where a light vortex is created due to the stirring of the mixture. It is important to ensure that the

solution in contact with the electrode is thoroughly mixed. This can be achieved by efficient stirring.

7. The titrator will stop by itself when it reaches pH 8.2. Note the final readings. This is called the titre value which will be in form of tartaric acid in g/L. The repeatability of titration on same puree was observed with every alternate sample.

### **Precaution**

The stirring of the mixture is important but it should not be too fast, otherwise the stirrer vortex will suck in air bubbles and CO<sub>2</sub> or O<sub>2</sub> can disturb the titration.

#### **3.1.5.2 Total soluble solids**

Soluble solids measured by a refractometer include sugars, organic acids, soluble pectins, anthocyanins and other phenolic compounds, and ascorbic acid. Thus the correlation between soluble solids and sweetness is low in some cases. Plant breeders can benefit from availability of quick methods for measuring total sugars and titrable acidity in fruits of their advance breeding lines. Consumer acceptance of nectarine, peach, plum and pluot cultivars is related to soluble solids to titrable acidity in ripe fruits (Crisosto and Crisosto, 2005).

A refractometer is a device that measures a refractive index. The index of refraction is determined by how much the speed of light or sometimes sound waves is reduced inside the object you are measuring. Handheld refractometers, digital handheld refractometers, laboratory refractometers and inline process refractometers make up the four main types available for use. In addition to measuring the refractive index, refractometers are able to measure solid matter and specific gravity. The liquid on the prism plate should be free from bubbles or floating particles of pulp or other matter.

Total soluble solids were measured in each sample from each replicates using an Atago Palette PR-32 digital refractometer (Atago Co., Ltd, Tokyo, Japan) (Bianco *et al.*, 2010) in 2009 and 2010. However, initial measurements in 2007 were done with a handheld refractometer. The refractometer is standardized with distilled water. It contains inbuilt temperature compensation capability.

## Handheld refractometer

Different models of traditional refractometer have different internal scales on which to read fluid concentrations. Some instruments have specialized scales that indicate the exact mixture of the sample being tested, while others have an arbitrary unit of measure that works like a shorthand for refractive index measurements.

1. A drop of sample was placed on the measuring surface beneath the illuminator
2. While looking through an eyepiece the Viewpoint illuminator was pressed.
3. The reading was taken at the point where the contrast line (difference between light and dark areas) crossed the scale.



**Figure 3.2 Handheld refractometer** (Source : [www.misco.com](http://www.misco.com))

## Digital refractometer

On three types of refractometers there are plates designated for sample application. On handheld and digital handheld devices the plate will be on the opposite side of the eyepiece. On the laboratory devices the plate will be either to the left or the right of the display screen. An inline process refractometer is a continuous measurement device. There is a sensor placed in line with the fluid being tested. The sensor is coupled with a control box that has a digital screen to display the test results. Use a pipette to obtain the sample and place it on the plate. Then cover the sample with the covering device included with your refractometer. It is important for the sample to either be heated or cooled to the appropriate temperature. Twenty degrees centigrade is usually appropriate, but the user should be aware of the proper specifications for the substance being tested.

While using a digital handheld refractometer, push a button that will cause an internal LED light to shine. There may be a need to rotate the eye piece to bring the measurement pad into focus. The light passing through the sample will bend through this process, illuminating the result on the measurement pad.

Apricot samples used for measuring soluble solids were extracted in a uniform way to take into account natural differences in the distribution of soluble solids within the fruit for the species concerned. The extracted juices served as representative of the whole apricot. Apricots were divided into halves. Each half was measured to get a mixture of juice from different parts of the fruit. The juice was taken from two parts of the fruit (e.g.

longitudinal slices, equatorial axis area) in a first step and then the two readings for each individual fruit were averaged. In a second step the sum total of these readings was averaged (round to one decimal place) to give a mean figure.

### **Checking and re-calibration to zero**

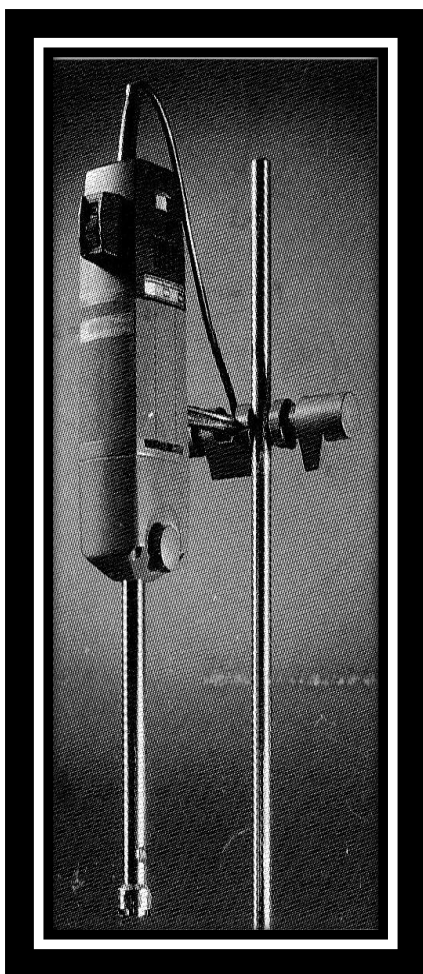
A bottle of distilled water and a bottle of 6 % sucrose solution were required. The solution was stored in a bottle, kept away from daylight and used within 48 hours of preparation.

Several drops of distilled water were placed on the prism surface. Distilled water should give a reading of zero. If not and where possible, the refractometer must be adjusted to read zero. The prism plate was wiped dry with a soft tissue free from fluff. Several drops of 6% sucrose solution were placed onto the clean and dry prism plate. The refractometer should give a reading of 6%. If the reading is not accurate:

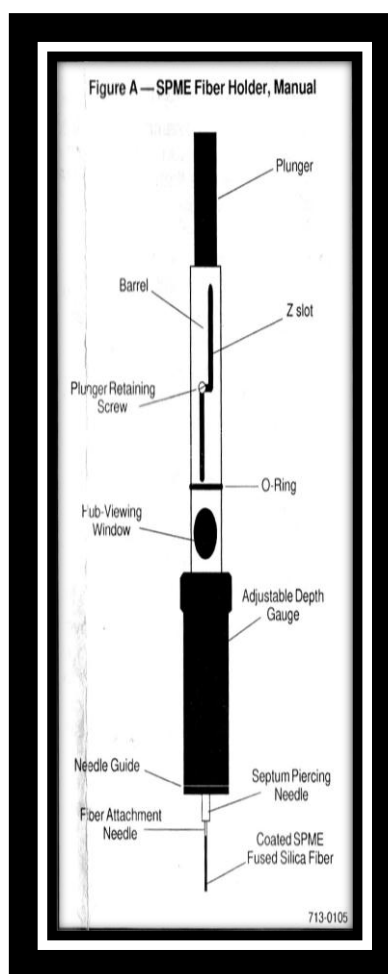
a) A new fresh solution of accurate 6% sucrose may be required. b) The refractometer may need to be repaired or replaced.

#### **3.1.6.1 Determination of apricot volatiles**

The volatile fraction was analyzed by headspace solid phase microextraction (HS/SPME) followed by gas chromatography/mass spectroscopy (GC/MS) modifying the protocol for peach (Agozzino *et al.*, 2007) and apple (Lo Bianco *et al.*, 2008). The frozen samples of six apricots were cut into small pieces. 50 gm of this homogenous sample were added to 50 ml of Ultra Pure (UP) water, in a cold bath and homogenized at high speed with Ultra Turrax (IKA® Works Asia Sdn Bhd, Serendah, Malaysia) with a shaft diameter of 10mm (Figure 3.3) for 30 s . This produces a homogenous puree, which was directly used for instrumental analysis. The fibers coated with 75µm carboxen/polydimethylsiloxane SPME fiber (Supelco, Bellefonte, PA, USA) were selected due to the function (F) of the sum of extracted analytes estimated by the fiber coating criterion function (Zuba *et al.*, 2002; Hamm *et al.*, 2003). The SPME holder for manual operation, and the fibers used in this investigation were from Supelco (Bellefonte, PA, USA) (Figure 3.1.7.2). Before first use the fiber was conditioned by insertion into the GC injector, which was kept at a suitable conditioning temperature for each fiber - 250°C for 1h for Carboxene/PDMS.



**Figure 3.3**  
Ultra Turrax® used for making  
apricot puree (Source: IKA®, Malaysia)



**Figure 3.4**  
SPME Holder with needle  
(Source: Supelco, USA)

### 3.1.6.2 Preparation of the sample

Prior to GC analyses, 5 gm of apricot puree sample was placed in 20 ml vial with Teflon coated silicone rubber septa and 25  $\mu\text{L}$  of a standard solution containing 0.948  $\mu\text{g}/\text{ml}$  of fenchone was added as an internal standard. 5 ml of saturated NaCl was added along with the magnetic stirrer and the vials were capped. The complete procedure until this step was done in an ice-bath. The system was moved to a hot water bath and placed on magnetic stirrer and heater. The SPME needle pierced the septum and the fiber was extended through the needle to bring the stationary phase into contact with the headspace of the sample. The vial was kept in a water bath with temperature maintained at 70°C for 15 min and the fiber was withdrawn into the needle as shown in **Figure 3.5** to reach equilibrium. The optimal time of HS saturation (15 min) was determined experimentally as it was suitable timing for fiber saturation and for reproducibility of extraction procedure.



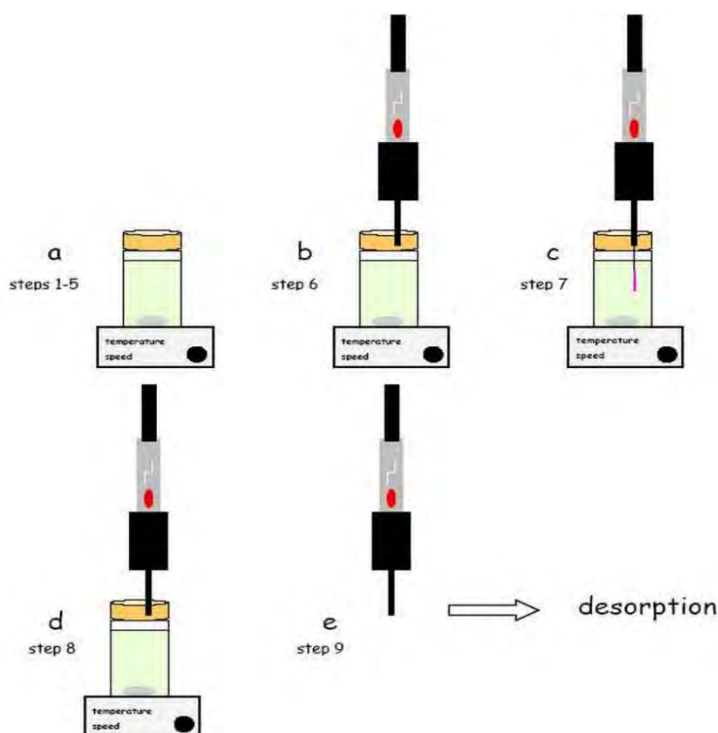


Figure 3.5

The extraction and desorption procedure

(Source: Risticvic *et al.*, 2010)

Before each micro-extraction, the fibers were cleaned to prevent carryover of high-boiling material. To that end, the fibers were inserted in the injection port, which was kept at the conditioning temperature of each fiber, for at least 20-30 min.

Finally, the SPME needle was removed from the vial and inserted in Hewlett Packard 5890 Series II gas chromatogram equipped with a flame ionization detector (FID), a split injection system for 10 min. Separation was performed by GC using a factor four <sup>TM</sup> Varian VF-5ms (Varian Inc.) capillary column of length 30 m and 0.25mm inner diameter and 0.25µm film thickness. Total analysis time was approximately 65 min, including 10 min for both equilibrium and sampling. Each sample was analyzed in triplicate.

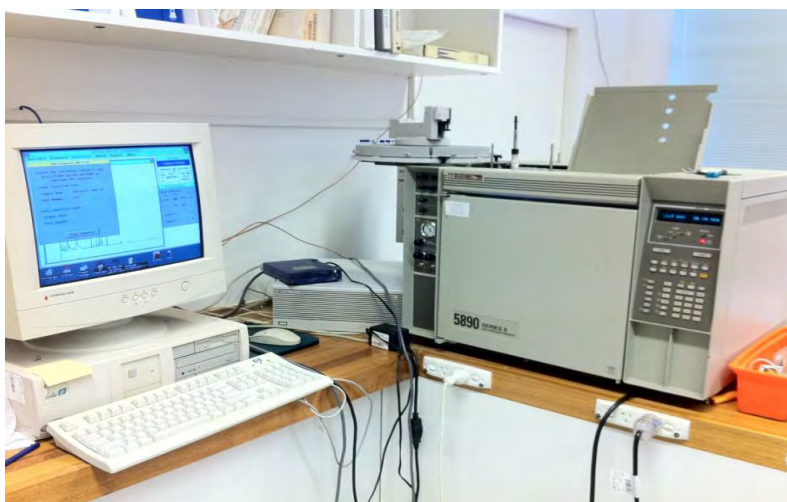
The technique as described was selected after successive attempts of extracting volatiles from samples at different temperature. The main thing to note was that the samples were frozen due to the need to store the large number of samples produced by the trials. To get the desired output of volatiles the temperature was kept at 70°C. The technique was selected from Solis-Solis *et al.*, 2007 except that it was modified with a change of temperature from 40 °C to 70 °C. Headspace sampling was done at 40 °C, 50 °C and 70 °C but the attempts to use lower temperatures were unsuccessful with the GC used. 70 °C was used to reduce artefact formation. The purees were made to break cells and enhance the availability of more volatiles to absorb on SPME fibres. Purees give maximum exposure of volatiles to the fibre rather than intact fruit or fruit slices particularly after there has been a need for frozen storage and long exposure times are not possible due to risk of breakdown.



### 3.1.6.3 GC conditions

The following GC conditions were used;

1. The carrier gas was instrument grade Nitrogen at a flow rate of 1.8 ml/min, a head pressure of 70KPa and a split ratio of 1:50.
2. The oven temperature changed with chromatography time according to the temperature program. However, the initial temperature ramp was 40° C for 4 min and then increased to 250 °C at 4° C/ min at first level, followed by the ramp to 290° C at 7° C /min for the second level and then maintained for 5 min at this final temperature.
3. Hydrogen and air column flows for the FID were 40ml/min and 200ml/min respectively
4. Injection port and the detector temperatures were 280° C and 300° C respectively.



**Figure 3.6 Gas Chromatograph with inserted SPME needle**

Collected data were processed with the instrument data system, and chromatographic and spectrometric results showed excellent reproducibility (Standard deviation  $\leq 5\%$ ). All standard reagents used; namely, 1-hexanol, hexyl acetate, ethanol were purchased from Sigma Chemical Company (St. Louis, Mo, U.S.A) and Fenchone (purity > 99%) was purchased from Fluka (Buchs, Switzerland).

Linear Retention Indices (LRIs) were calculated using Kovats' equation (Kovats, 1958) and a sequence of linear hydrocarbons from C<sub>6</sub> to C<sub>18</sub>. Apricot volatile compounds were identified first by a critical and reasoned comparison with mass spectral data within the NIST (Mass Spectral Database, 2008) 2008 library. Semi quantitative determination was carried out by the internal standard method. For perfect quantification each peak would be quantified against a standard of the specific compound.

## 3.2 Boron and other mineral analysis

Elemental composition data of dried apricot tissue was important to know the absorption of Boron in different parts of the tree at different time intervals. The determination of trace elements in complex matrices, such as dried apricot tissues, often requires extensive sample preparation or extraction regimes prior to instrumental analysis. Flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma optical emission spectrometry (ICP-OES) are the main techniques used for the determination of trace elements.

Apart from instruments that achieve good analytical results, the dexterity of the analyst and sample preparation methods employed for B determination have significant roles in accuracy and precision of analytical results.

The traditional techniques of dry ashing and wet ashing for sample preparation are time consuming and require large amounts of reagents, which are expensive, generate hazardous waste and might contaminate the sample with the analytes. Advances in sample preparation over the last few decades have been propelled by the advance of microwave assisted acid digestion (Arruda, 2007; Sneddon *et al.*, 2006; Buldini *et al.*, 2002), ultrasound assisted extraction and slurry preparation (Luque de Castro and Capote, 2007), and direct solid sampling analysis (Kurfurst, 1998). However, for our experiment we used wet ashing techniques due to easy accessibility to the reagents and instruments.

Boron deficiency is a potential problem in stone fruit production. Plant analysis can be helpful for diagnosing deficiencies, which are easily detected by leaf, branch and fruit analysis. Despite the developments in B determination techniques, some areas needed improvement in the technique. Boron tends to adhere to the sample introduction system of the analytical instruments and hence raise the background, affecting subsequent determinations. This phenomenon called memory effect presents a major problem in B analysis, especially if a sample containing low B concentration follows a high concentration sample.

The application of ICP-OES brought a significant improvement in boron analysis because of its simplicity, sensitivity and multi element detection capability. The plasma source OES provided higher sensitivity and lower detection capability for B determination that was not possible by spectrophotometer; flame AES/AAS and neutron activation methods. The development of ICP-OES revolutionized the analysis of several so called problem elements such as B, S, Mo and all hard to detect trace elements by virtue of its low detection limits, large linear range, multi element detection capability.

The detection limit and precision for B determination by ICP-OES are better than all previous methods (Sah and Brown, 1997). The decomposition of apricot plant materials was done with the wet ashing technique as it was easily accessible. The use of B containing digestion containers such as borosilicate glass was avoided to prevent B leaching from the container. To start with the first trial HNO<sub>3</sub> was used for wet ashing as it provides simpler matrix than other mineral acids.

### **3.2.1 Measurements and observations**

The leaves, branches and leaf for each treatment of boron and ReTain® were collected four times in the last two seasons. Total fruit yield was measured on the fourth harvest date when fruit were ripe for picking. Three leaves with petiole attached from each plot were collected after 24 hours of each spray. Seven fruits from each tree were collected from each harvest making a total of 24 replicates from each treatment. 12 fruits were analyzed for physical and chemical properties and the other 9 were used for determination of volatile compounds. 22 samples from selected nine treatments from sixteen different boron and ReTain® treatments making a total of 198 apricots were used for consumer perceptions.

Leaves, branches and fruit were washed in distilled water and blotted dry. Leaf and branch samples were dried in a forced draft oven at 70°C for 48 hours. Finally the dried leaves were ground with a grinder and packed in a plastic container and forwarded to CSBP Soil and Plant analysis Laboratory (Western Australia) for mineral analysis.

Freeze drying is regarded as the gentlest method to preserve plant material for analysis of various organic substances. The technique involves freezing the fruits, followed by placing them under reduced pressure, while supplying sufficient heat to sublime the ice. Apricot fruits were dried with the freeze dryer at -60°C for 48 hours to obtain dry weight for ICP-OES. The fruit samples were collected after 25 days, 50 days, 75 days and 100 days of flowering for all four concentration of boron.

### **3.2.2 Method development for boron analysis**

All chemicals were of analytical grade. Ultrapure water was obtained from the Central Science laboratory, UTAS, Tasmania. Suprapur nitric acid and hydrochloric acid (Merck, Germany) were used. All the glasswares used in experiment were kept in 10% w/v nitric acid solution for 12 hours before the experiment. Before the use of glassware it was rinsed with deionised water and dried in a dust free environment.

The type of acid used in the preparation procedure can have important consequences in the measurement step. It is observed that in all atomic absorption

techniques nitric acid is a desirable reagent. In spite of occasionally observed signal suppression in its presence as in ICP-OES, no severe analytical problems are encountered in practice with nitric acid at the concentrations of 10%. Sulfuric acid is usually avoided because of its high viscosity. Its presence is usually undesirable in analytical techniques where the sample introduction is by nebulization (FAAS, ICP OES, and ICP-MS) (Maria *et al.*, 2008). Novozamsky *et al.* (1993) suggested the use of  $\text{HNO}_3$ ,  $\text{HClO}_4$  and hydrogen peroxide for decomposition of plant materials.

Numerous preliminary experiments were carried out to confirm the validity of the techniques reported for the extraction of boron from plant tissues. The preliminary investigation resulted in confirming that nitric acid as the most effective to extract boron from apricot plant tissues.

### **3.2.2.1 Trial 1**

A mass of 100 mg of dried apricot tissue sample was weighed in a 20 ml test tube. 5 ml of nitric acid and 5 ml of water was added to it. The slurries were homogenized for 12 hours and digested on a hot plate for 3 hrs at 95 °C. Blanks were prepared in the same way as the sample using sugar, which presents boron concentrations lower than the quantification limit of the proposed method. All samples were analyzed in triplicate. Elements to be measured were determined in the final solution by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results were confusing and reflected interference of Boron either from glass wares or from the reagents used.

### **3.2.2.2 Trial 2**

As a result of issues with the first analysis, another experiment was designed to test purity of the nitric acid and water. The methodology was the same replacing the above experiment with HP nitric acid and HP water. The results proved that the laboratory reagents were appropriate to use for future tests and there might be a need to change the method for apricot samples.

### **3.2.2.3 Trial 3**

The method was optimized using univariate methodology. First slurries were prepared using 1.0, 2.0, 3.0 and 4.0 mol L<sup>-1</sup> solutions of nitric acid and hydrochloric acid. Nitric acid showed good results for copper and manganese whereas for iron the hydrochloric acid showed more efficiency. 5 ml of nitric acid and 5 ml of 30% (v/v) hydrogen peroxide was added to it. The samples were hold in fume cupboard for 12 hours and digested on a hot plate for 3 hrs at 95°C for complete digestion. The solution was cooled down and brought to final volume of 10 ml. It was properly sealed with paraffin and

forwarded to Central Science Laboratory to process with ICP-OES. However, even with the latest technology B was difficult to detect with this method. The results of this methodology were similar to trial experiments of Silva *et al.*, (2008).

However, wet ashed samples do not allow the *in-situ* material to be clearly distinguishable due to the aggregation of residual matter that apparently had not been fully oxidized. This implies that a combination of regular monitoring and chemical adjustment to suit apricot samples during preparation is necessary to achieve satisfactory results with the wet ashing process. The ability of some plants to withstand the wet oxidation process has previously been recognized as a problematic area (Pearsall, 1989).

The presence of substances such as high salts, organic substances and other analyte species may cause interference in boron determination. There are also chances of matrix related ionization suppression and mass discrimination causing errors in boron determination by OES and MS methods (Gregoire, 1987; 1990).

#### **3.2.2.4 Trial 4**

In this final experiment, 100 mg of powdered apricot tissues of leaves, branches and fruits were weighed accurately and transferred in 50 ml Erlenmeyer flask. 5 ml of nitric acid and 5 ml of 30% (v/v) hydrogen peroxide was added to it. The samples were hold in fume cupboard for 12 hours and digested on a hot plate for 3 hrs at 95°C for complete digestion. The solutions were left to cool down to room temperature transferred to a calibrated flask and diluted to a final volume of 10 ml with 1.0 mol L<sup>-1</sup> nitric/hydrochloric acid solution.

Blanks were prepared in the same way as the sample using sugar, which presents measured element concentrations lower than the quantification limit of the proposed method. All samples were analyzed in triplicate. Analysed elements were determined in the final solution by inductively coupled plasma Atomic emission spectroscopy (ICP-AES). The results were successful and boron was detected with the technique. However, processing a large amount of samples in a realistic given time with infrastructure provided was difficult. As result, the dried samples were forwarded to CSBP Soil and Plant Analysis laboratory for the detection of treatment effect of boron and other plant nutrients from different plant organs of apricots.

### 3.3 Experimental design

#### 3.3.1. Background of Qew orchard

The trials were conducted on a commercial property in Tasmania, “Qew Orchard” within commercial plantings. Qew orchard is located in the South East corner of Tasmania, within the Coal River Valley, which is recognized as a unique region for producing quality apricots in Tasmania. The valley, with its alternating cool nights and sunny days enjoys a micro climate ideal for the growing of fruit. The fruit are encouraged to sit on the tree longer to accumulate more sugars and less water weight. The climate and secure irrigation supply combined with good soil management enables the orchard to produce good quality food. The diversity of soil types found within the boundaries of the orchards requires advanced management (pruning, fertigation, foliar fertilizers application) techniques, in particular about irrigation.

**Table 3.1 Nearest Meteorological station and station climate data**

Station located approximately 5km from Qew Orchards (Australian Bureau of Meteorology data.)

Station ID								Latitude	Longitude		Height				
094212	CAMPANIA (KINCORA)							-42.69	147.43		45.0 m				
Statistics	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual	Years	
	Temperature														
	Mean maximum temperature (°C)	24.1	23.8	22.1	18.8	15.9	13.7	13.1	14.4	16.1	17.8	20.7	22.7	18.6	2000
	Mean minimum temperature (°C)	11.3	11.1	9.9	7.3	5.7	3.7	3.2	4.2	5.2	6.4	8.6	9.8	7.2	2000
															2011
Rainfall															
Mean rainfall (mm)	37.4	34.1	36.5	39.2	26.1	43.5	33.7	55.6	49.0	40.5	41.7	35.5	471.5	2000	
Decline 5 (median) rainfall (mm)	16.0	33.8	22.4	39.6	24.4	35.1	29.2	50.2	36.7	37.8	41.8	34.6	460.2	2000	
Mean number of days of rain ≥ 1 mm	4.8	4.9	6.5	5.9	6.0	6.3	7.0	8.2	9.3	9.1	6.9	5.6	80.5	2000	
														2011	

The apricot trees at Qew are planted in mounded soil and Tatura trellises, allowing the land to be left untilled and reducing the risk of over watering. Water is provided with drip irrigation and there are two systems of moisture monitors. M-Bug and AquaLink loggers are utilized on the properties. These are fully computerized moisture feedback systems that monitor soil moisture via electrical resistance.

Much of irrigation is done at early morning or night to reduce water evaporation. The system holds several weeks of readings providing continuous soil content data as well as accurate weather, soil and crop information.

Qew orchards grew ten varieties of apricots in 2007 at the start of the project. In 2010 due to consumer demand and high quality of fruit it was increased to thirteen different varieties. In terms of tonnage about half of the production is of European varieties and about half are of Canadian varieties. Fruits are handpicked with seasonal harvesters and immediately cooled in cold storage to reduce microbial infestations and ripening progress. The grading and packing process is carried out by Qew orchards themselves. There is a large handling, grading & packing shed in the orchard. Qew orchards supplies fresh apricots directly to major supermarket chains around Australia and to consumers through door sales and at country markets. There are 150,000 trees producing anywhere between 600 and 1200 tonnes of fresh apricots primarily for a mainland domestic market with a small proportion sent to the UK. Qew orchards recently introduced red pears to replace an unsuccessful apricot variety. It offers an opportunity to explore new market opportunities and use processing and storage facilities during the off season for apricots.

The experimental field work started in July 2007 and continued until January 2010. In 2008 due to heavy frost on in October, there was a huge amount of fruit loss in the experimental site. Moreover, there was below average rainfall combined with increased demand on supply of water to the Valley, the Craigbourne dam (the major source of irrigation water to the orchard) dried up. The water from a new replacement supply from Hobart water, additional lease storage, doubling of on-site storage and water supplied from a nearby private supply made sufficient irrigation water available for the season in 2008 to maintain trees but not to achieve maximal yields and quality. As a result, the project was extended for another year and experiments were continued. In mid 2010, Qew orchards were leased to the Apricot Cool Climate Project.

### **3.3.2 Selection of the apricot varieties**

Physico chemical requirements are regularly established for every new variety (Lurol *et al.*, 2007). In Qew Orchards, efforts by the farm manager are aimed at ensuring a continuous improvement in the quality of apricots. Thus, the aim of the present study was to determine the effect of preharvest boron and ReTain® foliar sprays on apricot fruit quality using a range of determinants. All experiments were conducted in Qew orchards using standard cultural practices. Apricots were harvested manually, collected in cartons directly after harvest, and brought to the laboratory for physico-chemical analysis.



Few quality parameters such as fresh Weight, size and shape, firmness and color analysis was done from the same set of the fresh apricots on the same day. Fresh weight and dry weight were monitored at every sampling time. Dry weight was obtained by drying the fruits with freeze dryer for 48 hours. Analysis was done by methods mentioned in 3.1.1, 3.1.2, 3.1.3 and 3.1.5. Samples were kept in a freezer at -18°C for TA, SSC and flavor analysis as mentioned in 3.1.6, 3.1.7 and 3.1.8 respectively.

The selection of the three main varieties for the main study was done by screening ten different varieties based on their maturity periods and accessibility. The ten varieties were Averin, Golden sweet, Goldrich, Qew, Moorpark, Orangered® Bhart, Palysteyn, Rival, Solarmate and Sundrop. The 'Rival', 'Goldrich' and 'Orangered® Bhart' varieties were selected on the basis of their harvest timings and accessibility for experimentation within the standard orchard management. 'Orangered® Bhart' is an early harvested variety and 'Rival' and 'Goldrich' are late harvested varieties.

### **3.3.3 Experimental foliar spray program**

In 2009-2010 the experiment was carried out in Qew orchards, Tasmania on 7 year old apricot (*Prunus armeniaca* L.) trees on Rival and Goldrich varieties (butt diameter about 110mm) and 5 year old Orangered® Bhart variety (butt diameter about 90mm). Buffer trees were kept in between the treated trees. 48 trees of each variety were selected and divided into four blocks. Each block consisted of 12 trees. The trees were planted with a spacing of 5 m between rows and 2.50 m within rows (1200 trees per hectare) on a sandy loamy soil with pH5.5 (measured in 1 M KCl solution). The soil is potassium and phosphorous deficient. Due to high magnesium levels inherent in the soils of Qew orchards, external lime is applied. As soil pH varies between different blocks the quantity of lime application varies.

For this experiment, treatments consisted of four sprays of different concentrations of boron in the form of Solubor (20% boron) followed by ReTain® (Valent Biosciences, USA). ReTain® was applied as an aqueous solution, containing 0.05% (v/v) of a non-ionic surfactant (Silwet L-77®, ABG-7011, Valent Biosciences). Trees sprayed with water served as controls. The study was conducted using a randomized complete block design with three replicates (as indicated in Figure 3.7). The sprays were applied at different developmental stages of the trees according to the BCCH general scale (Table 3.3). All sprays were applied in cool weather either in the early morning or late afternoon and evening by hand pressure sprayer at 1000L of water per hectare. Over 2 years the same trees with the same treatments were used for the studies. In each harvest, four random fruit from each tree were collected from the central zone of the tree crown.



Row		Column 1	Column 2	Column 3	Column 4
1	ReTain <sup>®</sup> treatments				
2	R0	R0B0	R0B3	R0B3	R0B2
3		Buffer			
4		R0B2	R0B0	R0B1	R0B3
5		Buffer			
6		R0B1	R0B2	R0B0	R0B1
7					
8	R1	R1B3	R1B0	R1B2	R1B1
9		Buffer			
10		R1B0	R1B1	R1B1	R1B2
11		Buffer			
12		R1B2	R1B3	R1B0	R1B3
13					
14	R2	R2B1	R2B2	R2B0	R2B2
15		Buffer			
16		R2B3	R2B0	R2B3	R2B3
17		Buffer			
18		R2B0	R2B1	R2B2	R2B1
19					
20	R3	R3B0	R3B1	R3B2	R3B3
21		Buffer			
22		R3B2	R3B3	R3B1	R3B2
23		Buffer			
24		R3B3	R3B0	R3B0	R3B1

### Concentrations of Treatments

#### Solubor

B0=1.2 Kg / ha

B1= 1.8 Kg/ ha

B2= 2.4 Kg/ ha

B3= 3.0 Kg/ ha

#### ReTain<sup>®</sup>

R0= Water (control)

R1 = 0.40 Kg/ ha

R2= 0.65 Kg/ ha

R3= 1.00 Kg/ ha

**Figure 3.7 Plot layout of the experimental design**

During the experiments, thinning of fruitlets or flowers was not done because it was assumed that the studied spray treatments might increase fruit yield. Protections against pathogens and pests were carried out according to standard recommendations for commercial orchards (Olszak and Bielenin, 1999).

In 2007 foliar sprays of four different concentration of Boron were applied to all three varieties of apricots with 4 replications (n=48) each. For both the year of 2009 and 2010, harvest days of Rival (n=192) and Goldrich (n=192) were picked on a single day in January while Orangered<sup>®</sup> Bhart (n= 192) was harvest 2 weeks earlier (third week of December) as it is an early harvested variety. A detail description of each experimental set up is given in Chapter 4.

The BBCH-scale (Table 3.2) is a scale used to identify the phenological development stages of a plant. Phenological development stages of plants are used in a number of scientific disciplines (crop physiology, phytopathology, entomology and plant breeding) and in the agriculture industry (timing of pesticide application, fertigation and agricultural insurance). To assist in use of the scale from year to year and across varieties maturing at different times I developed a photographic version of the scale (Table 3.3) for apricots in Tasmania (BBCH). This may be of use to others in future years and locations and has been provided to the Qew orchard manager. The abbreviation BBCH derives from Biologische Bundesanstalt, Bundessortenamt and **C**hemical industry. Unofficially, the abbreviation is said to represent the four agrichemical companies (**B**ayer, **B**ASF, **C**iba-Geigy and **H**oechst) that sponsored the initial development of the system.

### 3.3.3.1 BBCH-identification keys of stone fruit

The phenological stages of apricot trees, describing the different growth stages using the traditional nomenclature (Baggiolini, 1952) as well as the BBCH code (Lancashire *et al.*, 1991) is presented in Table 3.2. The BBCH-scale uses a decimal code system, which is divided into principal and secondary growth stages, and is based on the cereal code system (Zadoks scale) developed by Zadoks (1974). This information will improve the cultivation of apricots in Tasmania by expressing the timing of most agricultural operations on a standardised scale.

**Table 3.2 Phenological growth stages and BBCH-identification keys of stone fruit description**

(Meier *et al.*, 1994)

Code	Description
<b>Principal growth stage 0: Sprouting/Bud development</b>	
00	Dormancy: leaf buds and the thicker inflorescence buds closed and covered by dark brown scales
01	Beginning of bud swelling (leaf buds); light brown scales visible, scales with light colored edges
03	End of leaf bud swelling: scales separated, light green bud sections visible
09	Green leaf tips visible: brown scales fallen, buds enclosed by light green scales
<b>Principal growth stage 1: Leaf development</b>	
10	First leaves separating: green scales slightly open, leaves emerging
11	First leaves unfolded, axis of developing shoot visible
19	First leaves fully expanded
<b>Principal growth stage 3: Shoot development<sup>1</sup></b>	
31	Beginning of shoot growth: axes of developing shoots visible
32	Shoots about 20% of final length
33	Shoots about 30% of final length
	Stages continuous till . . .
39	Shoots about 90% of final length
<b>Principal growth stage 5: Inflorescence emergence</b>	
51	Inflorescence buds swelling: buds closed, light brown scales visible
53	Bud burst: scales separated, light green bud sections visible
54	Inflorescence enclosed by light green scales, if such scales are formed (not present in all cultivars)
55	Single flower buds visible (still closed) borne on short stalks, green scales slightly open
56	Flower pedicel elongating; sepals closed; single flowers separating
57	Sepals open: petal tips visible; single flowers with white or pink petals (still closed)
59	Most flowers with petals forming a hollow ball

**Principal growth stage 6: Flowering**

- 60 First flowers open
- 61 Beginning of flowering: about 10% of flowers open
- 62 About 20% of flowers open
- 63 About 30% of flowers open
- 64 About 40% of flowers open
- 65 Full flowering: at least 50% of flowers open, first petals falling
- 67 Flowers fading: majority of petals fallen
- 69 End of flowering: all petals fallen

**Principal growth stage 7: Development of fruit**

- 71 Ovary growing; fruit fall after flowering
- 72 Green ovary surrounded by dying sepal crown, sepals beginning to fall
- 73 Second fruit fall
- 75 Fruit about half final size
- 76-77 Fruit about 60% and 70% consecutive of final size
- 78 Fruit about 80% of final size
- 79 Fruit about 90% of final size

**Principal growth stage 8: Maturity of fruit and seed**

- 81 Beginning of fruit coloring
- 85 Coloring advanced
- 87 Fruit ripe for first picking
- 88 Fruit ripe for harvest
- 89 Fruit ripe for consumption: fruit have typical taste and firmness

**Principal growth stage 9: Senescence, beginning of dormancy**





- 91 Shoot growth completed; foliage still fully green
- 92 Leaves begin to discolor
- 93 Beginning of leaf fall
- 95 50% of leaves discolored or fallen
- 97 All leaves fallen
- 99 Harvested product






1 From terminal bud







### 3.3.3.2 BBCH-scale






The BBCH-scale (Table 3.3) identifies the phenological development stages of stone fruit (cherry = *Prunus cerasus* L., plum = *Prunus domestica* sp. *domestica*, peach = *Prunus persica* L., apricot = *Prunus ameriaca* L.). It is a plant species specific version of the BGCH-scale.

**Table 3.3 Phenological Growth Stages of 'Rival' and 'Goldrich' apricot trees according to BBCH**

BBCH Scale Code	Description	Photographs	Time of the year (Tasmania)
<b>0</b>	<b>Growth Stage 0 Sprouting/Bud development</b>		
<b>00</b>	Dormant Bud Stage: Figure 3.3.1 Absence of Swelling. Figure 3.3.2 End of leaf bud swelling, scales separated.	  <p>Figure 3.3.1      Figure 3.3.2</p>	May & June
<b>1</b>	<b>Growth Stage 1 Leaf development</b>		
<b>1</b>	Leaf Development Stage: Fig 3.3.3 Green scales slightly opens and axis of developing shoot visible. Fig 3.3.4 Different developmental stages of leaf.	  <p>Figure 3.3.3      Figure 3.3.4</p>	<p>September - December for first leaf</p> <p>The leaves remain on trees until April.</p>

<b>5</b>	<b>Growth Stage 5 Inflorescence development</b>		
<b>51</b>	<p>Bud Swell Stage: Figure 3.3.5 Swollen buds becomes prominent and absence of green tissues.</p>	 <p>Figure 3.3.5</p>	July
<b>53</b>	<p>Red Tip or Bud Burst Stage: Figure 3.3.6 The top of the bud has opened and the red color of the sepals is visible.</p>	 <p>Figure 3.3.6</p>	<p>August</p> <p>Week 1 &amp; Week 2</p>
<b>57-59</b>	<p>White Bud Stage: Figure 3.3.7 and Figure 3.3.8 The bud continues to open and the white petals are visible. This is sometimes called popcorn.</p>	 <p>Figure 3.3.7</p>  <p>Figure 3.3.8</p>	<p>August</p> <p>Week 3 &amp; Week 4</p>
<b>6</b>	<b>Growth Stage 6 Flowering</b>		
<b>60-64</b>	<p>First Bloom Stage: Figure 3.3.9 The flowers are half open.</p>	 <p>Figure 3.3.9</p>	<p>September</p> <p>Week 1</p>

65	<p>Full Bloom Stage: Figure 3.3.10 Figure 3.3.11 All or most of the flowers on the tree are open. When 50 % of flowers are open the first petals falling starts.</p>	  <p>Figure 3.3.10      Figure 3.3.11</p>	September Week 2
67	<p>Petal Fall Stage: Figure 3.3.12 The petals eventually falls leaving the sepals, stamens and ovary.</p>	 <p>Figure 3.3.12</p>	September Week 3
69	<p>In the Shuck Stage: Figure 3.3.13 When all the petals have fallen and the shuck hides the fruit. The shuck is formed by the floral cup, composed of the fused sepals.</p>	 <p>Figure 3.3.13</p>	September Week 4
7	<b>Growth Stage 7 Development of Fruit</b>		
72	<p>Fruit Development Stage: Figure 3.3.14 Growth of the fruit eventually splits the shuck open. Figure 3.3.15 A small fruitlet developing from shuck.</p>	  <p>Figure 3.3.14      Figure 3.3.15</p>	October Week 1 & Week 2

<p><b>73-79</b></p>	<p>Figure 3.3.16 A 4mm to 24 mm fruitlet Fruit thinning-Stage 4. Pit hardening -Stage 5.</p> <p>Figure 3.3.16 B 25 mm to 1" fruit Stage 8- Half size of fruit.</p> <p>Figure 3.3.16 C 1.0" to 3" Fruit Stage 15- Full size fruit.</p>	<p>A</p>  <p>B</p>  <p>C</p>  <p>Figure 3.3.16</p>	<p>October- December</p>
<p><b>8</b></p>	<p><b>Stage 8 Maturity of fruit and seed</b></p>		
<p><b>81-87</b></p>	<p>Coloring Fruit Stage: Figure 3.3.17 The fruit color changes from green to yellow.</p>	 <p>Figure 3.3.17</p>	<p>November- December</p>
<p><b>89</b></p>	<p>Harvest Stage: Figure 3.3.18 The fruit is ripe and ready to harvest.</p>	 <p>Figure 3.3.18</p>	<p>January Week 1</p>



**Table 3.4 Boron and ReTain® Foliar Spray Program (Year -2009 and 2010)**

	Variety of Apricot	Common Name	Active Ingredient	No. of Sprays	Rate of Spray	Stage of the Tree	BBCH* scale identification
<b>Boron</b>	1. Rival 2. Goldrich 3. Orangered® Bhart	Solubor	20.5% Boron	4	B0=1.2 Kg / ha B1= 1.8 Kg/ ha B2= 2.4 Kg/ ha B3= 3.0 kg/ ha (of mixture)	1.) Before full bloom (at green and white bud stage) 2.) At petal fall stage after flowering 3.) 7 days after petal fall 4.) 21 days after petal fall	57 67  69 72
<b>ReTain®</b> (Plant Growth Regulator)	1. Rival 2. Goldrich 3. Orangered® Bhart (applied only in 2010)	ReTain®	150g/kg AVG (Aminoethoxyvinylglycine)	2	R0= Water (control) R1 = 0.40 Kg/ ha R2= 0.65 Kg/ ha R3= 1.00 Kg/ ha (of mixture)	5.) 14 days before harvest 6.) 7 days before harvest	87 88

\* BBCH = decimal growth stage for apricots in Tasmania see Table 3.3b.

## CHAPTER 4

### EFFECT OF BORON AND ReTain® ON QUALITY PARAMETERS OF RIVAL, GOLDRICH AND ORANGERED® BHART APRICOT VARIETIES

#### Abstract

Techniques to improve fruit firmness and quality in apricot would enhance marketability. Apricot is considered as one of the most delicious temperate fruits, and good balance of sugars and acids and a strong apricot aroma are the major determinants of exceptional fruit quality. The selection of the varieties for the main study was done by screening nine different varieties based on their maturity periods. A two year field studies were conducted in three different varieties of apricot (*Prunus armeniaca* L.) namely 'Rival', 'Goldrich' and 'Orangered® Bhart' to determine whether pre-harvest foliar applications of different concentrations of boron and ReTain® influences fruit quality and fruit set.

Boron sprays improved the flower cluster numbers by 12-15% in Rival, 4-12% in Goldrich and 4-10% in Orangered® Bhart varieties. Boron successfully increased the flower buds and fruit set. ReTain® eliminated the effects of Boron. The treatment responses of all three varieties were significantly different and the relative measured quality parameters for the varieties across two successive years were different. This indicated the treatments were investigated across a wide range of environments allowing testing for generalized responses.

Specific treatment results indicated that the titrable acidity and pH had slight consistent decreases with the combined addition of boron and ReTain® treatments for both years. Firmness was of specific concern as fresh apricots have a very short shelf life of only five to six days and transfer of fruit from farm to market within limited time span is a major concern. Firm fruit with adequate sweetness would allow Tasmanian orchardist to export more fruit. ReTain® improved the firmness of 'Rival' and 'Goldrich' varieties from 10-20% and 6 – 29% respectively with decreases in sugars from 7 - 20% and 4-12%.

The boron levels at four different stages of spraying were measured with Induced Couple Plasma-Optical Emission Spectroscopy (ICP-OES). This was done in order to examine the absorption of boron in response to the foliar applications of boron in different parts of the tree such as leaves, branches and fruits. The results indicated maximum boron absorption of 13-48% in fruits of Goldrich followed by 13-

23% in fruits of Orangered® Bhart. Boron sprays did not affect the Nitrogen (N) and magnesium (Mg) in plant tissues.

Overall, the data indicated that boron could have physiological effects in the orchard and that both boron and ReTain® could significantly affect fruit quality in both general predictable ways as well as via complex interactions that are presently not clearly predictable. The data indicate a need to consider quality effects in any treatment carried out in the orchard.

## 4.1 Introduction

Boron is involved in numerous processes such as vegetative growth, tissue differentiation, and metabolic control through regulation of enzymatic reactions, membrane integrity and function, sugar translocation and many other functions (Marschner, 1995; Blevins and Lukaszewski, 1998). Until the late 20<sup>th</sup> century, the primary physiological role of boron remained unknown.

Improving the flavor, the most important quality parameter of fruit is the foundation for success in producing fresh apricots. A wide range of environmental and genetic factors affects apricot fruit quality, where nutrition plays an important role. Potassium (K), calcium (Ca) and boron (B) are the key nutritional factors controlling fruit development and maturation (Marschner, 1995).

The interaction of cation requirement, water relations and B nutrition has profound influence on fruit quality. Boron amelioration of fruit quality could be directly or indirectly related to an interaction of B and cation nutrition (Davis *et al.*, 2003). Boron utilization efficiency is associated with fruit maturation gene activity in a B species, but research is limited regarding the physiological role and mechanisms of B nutrition in fruit development (Xu *et al.*, 2001).

B has important effects in pollen germination and pollen tube growth. The viability of pollen grains also decreases when B is deficient. For most crops, 1-4 mg/Kg soil is sufficient to prevent nutrient deficiencies'. Less than 0.5 mg B/kg is rated as marginal to deficient. Production of fruit, nut and seed crops is adversely affected much more than vegetative growth with a low supply of available B in soil. Boron levels in boron-deficient plant tissue are < 5 ppm in less sensitive grass crops such as corn, sorghum, and wheat, and < 20 ppm in broadleaf crops such as soybeans.

Sensitive crops such as sugar beets, sunflowers, alfalfa, and some tree crops, are usually deficient when the boron tissue level is < 30 ppm. The adequate boron level for apricot is 20-60 ppm. B levels less than 15 ppm in leaves indicate a B deficient plant and more than 80 ppm is toxic to apricot trees (Reuter & Robinson, 1986). When B deficiency is severe, necrosis develops internally in the spurs, the leaves become pale green, narrow and cupped with marginal scorching at times and numerous sunken canker appear on the trunks and branches (Johanson *et al.*, 1955). Concentration of Boron (B), Copper (Cu), Iron (Fe), Magnesium (Mg), Manganese (Mn) and Zinc (Zn) was analyzed in fresh and dried fruit samples of nine different apricot cultivars. The data reports that the Boron contents of dried apricot samples were found to be in the ranges of 16.57 mg/kg-1 in “Goldbar” cultivar to 40.09 mg/kg-1 in “Tom cot” cultivar (Davarynejad *et al.*, 2012).

It has been reported that soil and /or foliar application of B can eliminate or reduce B deficiency and consequently improve the vigor and cropping of pear trees (Woodbridge *et al.*, 1952; Johnson *et al.*, 1955). Boron fertilization increased fruit yield of Italian prune (*Prunus domestica* L.), apple (*Malus domestica* L.) and peach (*Prunus persica* L.) trees, which were not considered deficient in B (Hanson and Breen, 1985; Kamali and Childers, 1970; Wojcik *et al.*, 1999). However, there is often no response to B fertilization for hazelnut (*Corylus avellana* L.) (McNeil *et al.*, 1997) and highbush blueberry (*Vaccinium corymbosum* L.).

Foliar boron sprayed at pre bloom stages of fruit crop supplies available B at the critical periods of pollen formation, germination and fertilization just prior to fruit set. Foliar applied boron is rapidly absorbed by the leaves and flower buds and is often applied repeatedly three to four times for maximum effects. The application ensures that flower buds have enough B to carry them through flowering, fruit set and later developmental stages.

Firmness and sugars are of specific concern as fresh apricot has a very short shelf life of five to six days and transfer of fruit from farm to market within specific limited time span is a major concern. Ethylene is involved in all stages of the ripening process: it triggers the activity of various enzymes responsible for flesh softening, ripening rate, color and sugar content as well as other processes, e.g. abscission (Tonutti *et al.*, 1991).

One option for improved shelf life is to develop strategies to regulate the ripening process on the tree and thereby slow down post-harvest decay. The manipulations of the ripening process were examined on peaches (*Prunus persica* L) by applying Aminoethoxyvinylglycine (AVG) and polyamines that inhibit ethylene (Bregoli and Costa *et al.*, 2002).

Aminoethoxyvinylglycine (AVG) is an amino acid that inhibits ethylene production by inhibiting the activity of ACC (1-aminocyclopropane-1-carboxylate) synthase, a rate-limiting enzyme in the ethylene biosynthetic pathway (Yang and Hoffman, 1984). AVG also delays fruit ripening (Bangerth, 1978) that in turns delays color development and fruit softening. AVG is the active ingredient of a new chemical ReTain® (Valent Biosciences, USA) that in field trial revealed to reduce fruit abscission and to improve fruit quality (Byers, 1997).

The delay of the ripening period is a critical step to maintain fruit firmness at harvest and is examined in different cultivars of apples (Whale and Singh *et al.*, 2008). Delay in ripening is based on subjective evaluation of acid and brix ration, color and higher flash firmness. In previous study AVG was evaluated for its efficacy in lowering metabolic activity and reducing the delaying of internal break down and in turn prolonged post-harvest life in pears (Bramlage *et al.*, 1980; Romani *et al.*, 1983; McGlasson *et al.*, 2005). However, there is no scientific evidence in the literature whether a combination of B and ReTain® could improve the quality of apricots.

In the present studies, boron and ReTain® were applied in the form of preharvest foliar sprays to manipulate the ripening process and improve fruit quality in a climacteric fruit under field conditions. The trees were sprayed at different times and developmental stages of apricots according to the BBCH general scale of Tasmanian apricots (Table 3.2 and 3.3). The sprays were used for three varieties of apricots namely Rival, Goldrich and Orangered® Bhart. The goal was to create firm fruit with adequate sweetness, which would allow Tasmanian orchardist to export more fruit.

The aim of this study was

1. To study the effects of boron on fruit set, fruit drop and flower buds for three cultivars of apricots for two seasons.
2. To examine the fruit quality responses of B and ReTain® application for three varieties of apricots namely Rival, Goldrich and Orangered® Bhart. The selections of the varieties were done by screening them from ten different cultivars.
3. To determine the effects of boron inputs on fruit status as well as tissue mineral concentrations during apricot growth and development in order to determine whether the application gave strength to the outer skin of the apricot and thereby improved the firmness of apricot.
4. To characterize the post-harvest changes in the physico-chemical properties and mineral nutrition of three varieties of apricot with boron and ReTain® treatments over two years.

## 4.2 Materials and methods

### 4.2.1 Boron treatments and design of the experiment

The experiments were carried out during 2009-2010 in a commercial orchard in Tasmania on 7 years old 'Rival', 'Goldrich' and 5 years old 'Orangered® Bhart' trees to study the effects of boron and ReTain® on quality parameters. The effect of boron treatments on fruit set, fruit drop at harvest and flower buds was experimented in 2007 and 2009, as there was heavy fruit loss in 2008 due to frost. Although the spray programs were performed completely, due to the lack of the samples on trees, the project was extended. The field trials were conducted at a local orchard (Qew orchard) in Tasmania. The physico-chemical properties of the soil from the surface horizon of (0-20 cm) were analysed. The details of experimental site and design are described in section 3.1. Thinning of flowers or fruitlets was not carried out during the experiment. Protection against pathogens and pests was applied according to the standard recommendations for commercial orchards (Olszak and Bielenin, 1999).

B and AVG were applied in the forms of Solubor (20% boron) and plant growth regulator ReTain®(AVG) .Over the two year duration of the experiment the same trees were used for the treatments under evaluation. The experiments were conducted using a randomized complete block design with three replications. A total of 12 experimental plots with 12 trees (in each plot) with same vigor and size were selected making 148 experimental trees for 16 different treatments. Planting density

was 400 trees/ hectare. The number of sprays and timing of sprays are listed in Table 3.4.

The different four treatments of boron and ReTain® are listed in Table 3.4 makes a 16 treatments including control. Trees sprayed with water served as control. It is important to note that although external B was not applied to the soil a very small amount of boron was already present in the system due to previous year fertilization application through fertigation. However, the amounts were too small to hinder the field trial. Whole tree treatments were applied by backpack sprayer equipped with a hand lance and were sprayed until the surfaces were just at the point of drip. A plastic shield was placed in between and behind apricot trees to prevent any spraying reaching other trees.

Preharvest drop in prunes consisted erratically drop of fruit throughout fruit development while normal fruit tend to drop during a few weeks as fruit mature. The total number of fruits at the time of harvest was counted individually on each tree. The total number of flowers on trees was counted. The number of fruits dropped down at the time of harvest was noted for one week continuously.

#### **4.2.2 Analysis of physico-chemical quality parameters of apricot**

Fruit quality traits such as fresh weight, color and fruit firmness were measured on fresh samples. Flesh firmness was measured on two opposite sides of each fruit using a Penetrometer fitted with 8 mm plunger for 12 replicates of same treatment. Visual color analysis was done for color. The same samples were frozen and used for total soluble solid contents (SSC) and titrable acidity. SSC was measured with an Atago digital refractometer and automatic titrator was used to measure pH and acidity of the samples. The titration was done with 0.01 N NaOH to pH 8.2 and expressed as malic acid equivalent.

For mineral analysis, three leaves with petiole attached from each plot and four small pieces of branches were collected 24 hours after each spray application. The leaves and branches were rinsed twice to remove external chemical with distilled water and were dried in a force draft oven at 70°C for 48 hours to analyse the mineral composition of treated samples. The samples were ground with commercial spice grinder for medium size fruit of equal weight and same ripening stage were collected four times during whole spraying program to note the status of mineral nutrition. The dry weight of fruit sample was obtained by drying the samples in freeze dryer at -60°C for 48 hours. The dried samples were forwarded to CSBP Soil

and Plant Analysis laboratory for the detection of treatment effect of boron and other plant nutrients from different plant organs of apricots. The detailed methodology for individual methods is discussed in Chapter 3.

#### **4.2.3 Statistical analysis**

Multivariate analysis of variance (MANOVA) was used to determine the effects of the four different boron treatments on flower buds and fruit set. Fruit size distribution, fruit weight, kernel weight, firmness, sugars, pH and acidity were analysed using Multivariate analysis with a General Linear Model ( $P < 0.05$ ). All analysis were performed with a statistical software program SPSS (SPSS Inc., Chicago, Ill., U.S.A.).



Table 4.1 Comparison of physico-chemical parameters for nine cultivars of apricot

	Fruit Volume (cm <sup>3</sup> )	Fresh Weight (g)	Kernel Weight (g)	pH	Brix (%)	Titrateable Acidity (g/L)	Sugar to Acid Ratio	Firmness (N)	Color
<b>Averin</b>	163.8c	87.2 <sup>c</sup>	3.87 <sup>b</sup>	3.86 <sup>cd</sup>	12.6 <sup>b</sup>	11.2 <sup>a</sup>	1.14 <sup>de</sup>	31.5 <sup>de</sup>	1
<b>Sundrop</b>	101.2ab	54.5 <sup>a</sup>	2.95 <sup>a</sup>	4.03 <sup>d</sup>	14.6 <sup>cd</sup>	9.9 <sup>a</sup>	1.53 <sup>f</sup>	22.0 <sup>bc</sup>	2
<b>Golden Sweet</b>	104.0ab	55.8 <sup>ab</sup>	3.73 <sup>ab</sup>	3.79 <sup>bcd</sup>	12.7 <sup>b</sup>	15.3 <sup>c</sup>	0.84 <sup>bcd</sup>	35.1 <sup>de</sup>	2
<b>Solarmate</b>	114.5b	65.8 <sup>a</sup>	3.85 <sup>a</sup>	3.85 <sup>cd</sup>	14.9 <sup>cd</sup>	14.5 <sup>bc</sup>	1.04 <sup>cde</sup>	20.8 <sup>bc</sup>	2
<b>Palsteyn</b>	87.0a	60.2 <sup>a</sup>	3.59 <sup>ab</sup>	3.69 <sup>bc</sup>	8.3 <sup>a</sup>	17.0 <sup>c</sup>	0.49 <sup>a</sup>	30.7 <sup>de</sup>	3
<b>Moorpark</b>	110.9ab	56.5 <sup>a</sup>	3.88 <sup>b</sup>	3.52 <sup>b</sup>	11.8 <sup>b</sup>	14.4 <sup>bc</sup>	0.75 <sup>abc</sup>	20.9 <sup>bc</sup>	1
<b>Orangered® Bhart</b>	104.9ab	58.1 <sup>a</sup>	3.22 <sup>ab</sup>	3.70 <sup>bc</sup>	13.4 <sup>bc</sup>	11.6 <sup>ab</sup>	1.25 <sup>ef</sup>	28.2 <sup>cd</sup>	4
<b>Goldrich</b>	209.4d	106.4 <sup>d</sup>	5.08 <sup>c</sup>	3.02 <sup>a</sup>	12.2 <sup>b</sup>	22.9 <sup>d</sup>	0.57 <sup>ab</sup>	36.2 <sup>e</sup>	2
<b>Rival</b>	144.0c	78.2 <sup>bc</sup>	3.11 <sup>ab</sup>	3.73 <sup>bcd</sup>	16.1 <sup>d</sup>	11.3 <sup>a</sup>	1.47 <sup>f</sup>	30.9 <sup>de</sup>	3
Data are the means of the determinations made independently in 12 fruits, Means with the same letter for each variable are not significantly different at $\alpha = 5\%$ Visual color analysis described in Figure 4.7									

## 4.3 Results

### 4.3.1 Quality traits for ten different cultivars of Tasmanian apricots

The selection of apricot varieties to use for the trial of boron and ReTain® sprays was done by analysing nine different cultivars for their physico-chemical properties and maturity dates. The fresh weight, volume, kernel weight, pH, visual color analysis, Brix and titrable acidity were measured according to the techniques described in Chapter 3. Resource constraints required color to be assessed visually.

#### 4.3.1.1 Evaluation of physical properties

Analysis of fruit physical attributes revealed significant variation among the 9 cultivars regardless of the ripening season. Peel color was a distinctive orange/red with a red blush in the Orangered® Bhart and Palsteyn varieties, dark orange in Rival and Solarmate, orange in Sundrop, Golden sweet, Solarmate and Goldrich, light yellow peel color was found in Averin. Though Moorpark apricots had a green color with a slight tint of orange color, the Brix was optimum for flavor.

Average fresh weight varied greatly ranging from 54 g to 106 g and fruit volume from 86 cubic cm to 200 cubic cm (Table 4.1). Among the nine cultivars, Sundrop exhibited below average fresh fruit weight, while Goldrich exhibited above average fresh fruit weight. The samples of Solarmate had a big variation in fresh weight ranging from 40 g to 78 g and therefore the volume was low compared to the other eight varieties.

#### 4.3.1.2 Evaluation of chemical properties

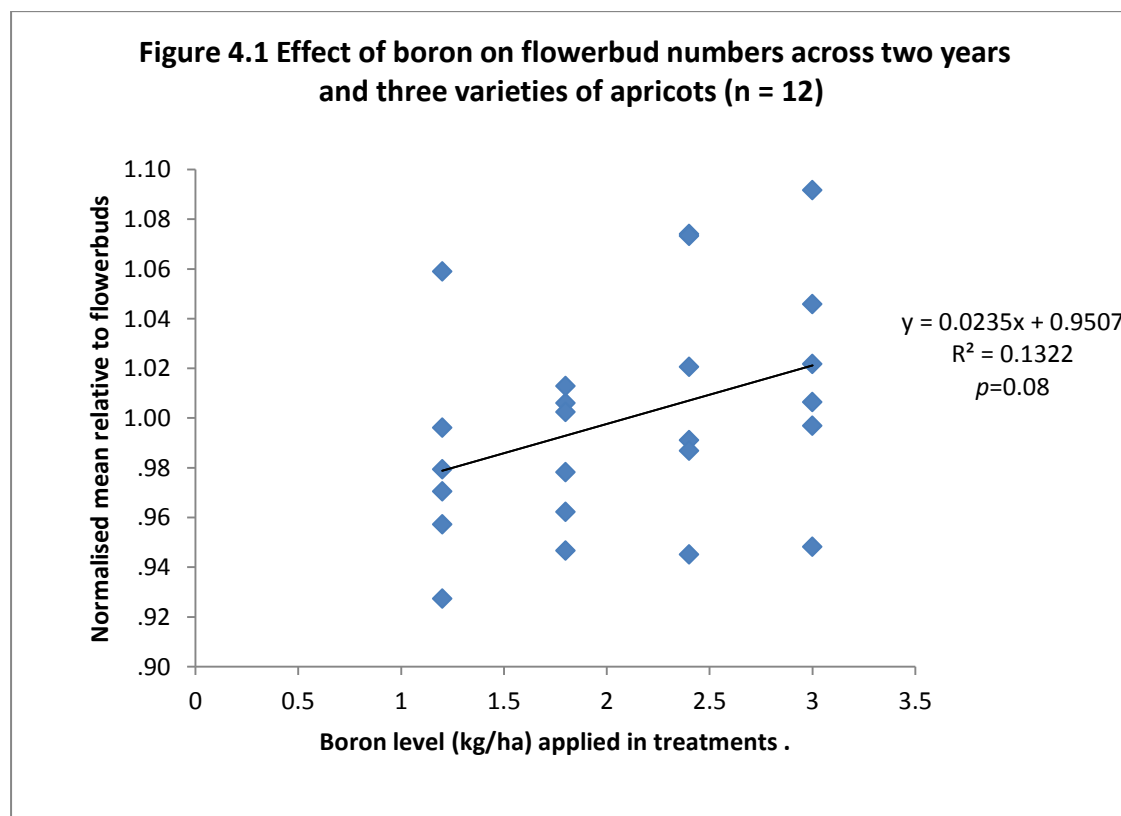
Chemical attributes, like the physical attributes, showed a great variation among cultivars but no differences specifically consistent with the ripening season. Juice pH ranged from 3.02 for Goldrich to 4.03 for Orangered® Bhart. Juice titratable acidity varied greatly ranging from 9.85 g/L in Sundrop to 22.88 g/L in Goldrich. Soluble solids were in the range from 8.25 for Palsteyn to 16.07 for Rival. The Palsteyn variety may not have qualified as having a superior level of sugars but the study of its volatiles profile could help in better understanding of its flavor. Sundrop and Solarmate had similar Total Soluble Solids (TSS) of ~14°Brix and Rival had the maximum amount of TSS at 16.98°Brix, which was highly significantly different from six out of eight of the other varieties. For Brix, Rival was not significantly different

from Sundrop and Solarmate. Goldrich was the firmest variety, significantly different from all the other seven varieties except Rival.

The selection of the varieties to use in the subsequent trials was done based on average firmness and availability of the fruits from the experimental site. As Rival and Goldrich were firm and intermediate harvested fruits, they were selected. Selection of the early harvested Orangered® Bhart was done to provide enough time to do laboratory analysis for all three selected varieties. Thus finally Rival, Goldrich and Orangered® Bhart were selected for further trials to analyze the effects foliar applications of boron and ReTain® sprays.

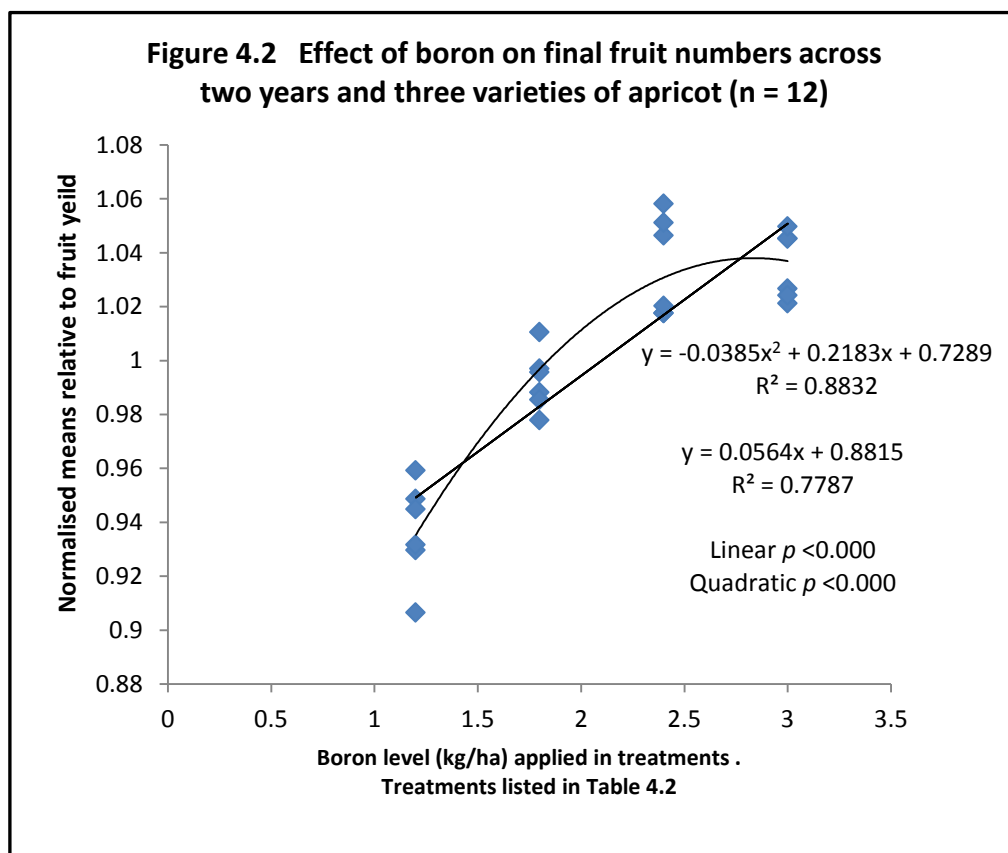
#### 4.3.2 Effect of boron on quality parameters of three cultivars of apricot.

Figure 4.1 describes the effects of boron on flower buds for three varieties of apricots over two years. The boron treatments increased total flowerbuds by up to 13% in Rival, ~ 10% in Goldrich and ~11% in Orangered® Bhart compared to the control. For Rival and Orangered® Bhart B2 treatments had the maximum effect on the amount of flowerbuds. The results were consistent for both the years. However, in Goldrich the B3 treatments had the maximum effects on the amount of flower buds.

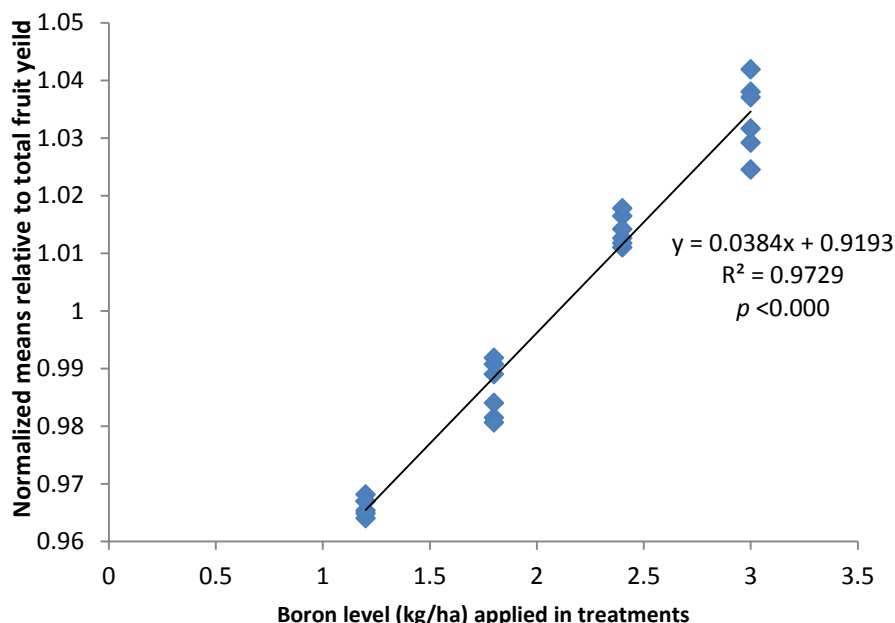


The results obtained here for flower bud numbers were not quite significant ( $P=0.08$ ) but are in agreement with those observed in other tree species, in which foliar B applications made immediately prior to flowering or during the period of floral bud initiation significantly increased flower buds as well as fruit set and yield (Wojcik, 2003). There was no significant correlation between effects of boron treatments and flower buds for any of the varieties of the apricots (Table 4.2). The foliar application of boron was done at the different times listed in Table 3.4.

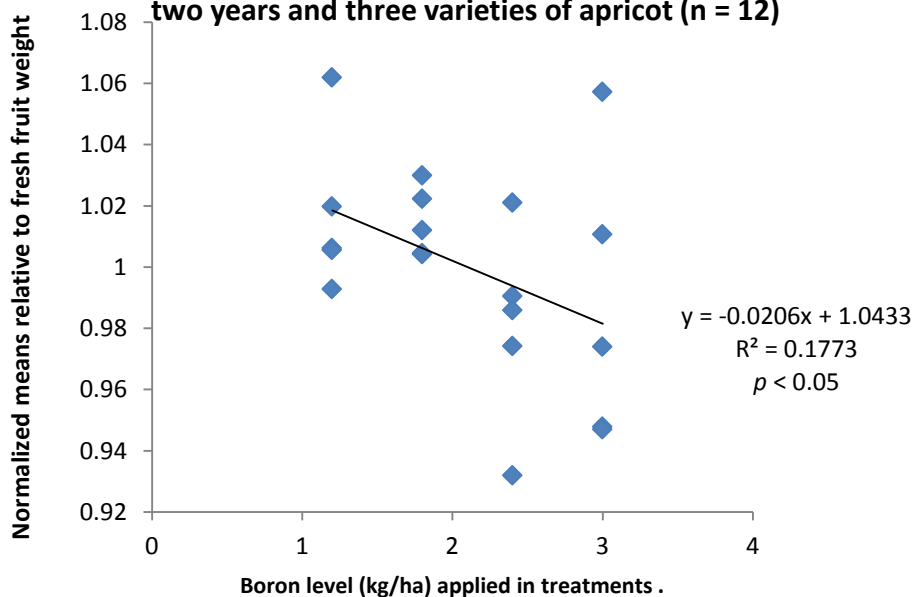
The increasing concentration of boron decreased the fruit drop of Rival by up to 7%, Goldrich by up to 32% and Orangered® Bhart by up to 47% percent. The results indicated that the varieties behaved somewhat differently for the effects of boron (Table 4.2). There is moderate linear regression for fruit drop and boron treatments ( $R^2 = 0.16$ ;  $P=0.054$ ). When a non linear regression is applied this improves significantly ( $R^2 = 0.58$ ;  $P<0.000$ ). Suggesting at the intermediate boron concentration across years and varieties fruit drop decreases while being higher at the lowest and highest concentrations.



**Figure 4.3 Effect of boron on fruit set numbers across two years and three varieties of apricot (n = 12)**



**Figure 4.4 Effect of boron on final fruit weight across two years and three varieties of apricot (n = 12)**



The fruit drop was decreased significantly in Orangered® Bhart and Rival variety for both the years. There was ~47% decrease in fruit drop in Orangered® Bhart and ~ 33% in Goldrich due to the effect of boron treatments for both the years. However, the effects of the concentration of boron used as treatment were different and specific for each variety. Fruit drop of Rival was very little affected by boron treatment compared to other two varieties.

**Table 4.2 Slope from linear regression equations and coefficients of determination ( $R^2$ ) comparing foliar boron application effects on flower buds and fruit yield of apricots for each variety across two years (2007-2009)**

	Rival			Goldrich			Orangered® Bhart		
	$R^2$	a	P- value	$R^2$	a	P- value	$R^2$	a	P -value
Flower Buds	0.37	11.39	0.39	0.06	3.56	0.75	0.8	6.45	0.11
Fruit Set	0.97	1.89	0.01*	0.95	1.64	0.02*	0.99	1.7	0.00*
Fruit Drop	0.96	0.18	0.02*	0.02	-0.14	0.85	0.62	-1.67	0.21
Final Fruit	0.98	2.08	0.01*	0.74	1.78	0.14	0.85	3.67	0.08

\* indicates significant at  $P \leq 0.05$

Fruit set was affected by B fertilization for all three varieties. There was a very strong, significant, linear response of fruit set to increasing boron overall (Figure 4.3,  $R^2 = 0.97$  at  $P=0.000$ ) and for each variety separately (Table 4.2). Increasing boron also significantly increased total final fruit numbers (Fig 4.2). The beneficial effects of foliar B application varied between treatments for each year.

There was a weak regression overall (Figure 4.5) for fruit size with increasing boron. The positive slope of the regression for final fruit number was 5.64% per kg extra boron while the negative slope for the regression of fruit size was 2.06% per kg extra boron. This indicates a positive yield effect of boron of approximately 3% per kg boron albeit with smaller, potentially less valuable, fruits. The boron treatments B2 and B3 were effective in improving the total fruit set for all three varieties of apricots.

### 4.3.3 Effect of boron on quality attributes of Rival, Goldrich and Orangered® Bhart cultivars of apricots

The main problem experienced when using boron sprays in the present study were inconsistent responses from site to site and from season to season. The fresh weight of apricots increased by up to 10% with the increase in concentration of boron compared to the control in 2010. However, in 2009, there was a decrease in fresh weight suggesting that the results were quite inconsistent across the two years. The same inconsistency of results was reflected in volume.

**Table 4.3 Mean values of physico-chemical parameters for apricots treated with different boron amounts, 2009/10 across four ReTain® levels (treatment n=42)**

YEAR	Boron Kg/ha	Fruit Fresh Weight (g)	Kernel Weight (g)	Volume (cm <sup>3</sup> )	pH	Brix (%)	Titration acidity (g/L)	Brix:acid ratio
2009	1.2	64.68 <sup>b</sup>	3.11 <sup>b</sup>	119.98 <sup>c</sup>	3.45 <sup>a</sup>	12.24 <sup>ab</sup>	13.79 <sup>a</sup>	1.00 <sup>a</sup>
	1.8	62.84 <sup>ab</sup>	2.99 <sup>ab</sup>	113.90 <sup>bc</sup>	3.45 <sup>a</sup>	12.21 <sup>ab</sup>	13.85 <sup>a</sup>	1.04 <sup>a</sup>
	2.4	61.68 <sup>ab</sup>	3.06 <sup>ab</sup>	109.00 <sup>ab</sup>	3.45 <sup>a</sup>	12.60 <sup>b</sup>	14.66 <sup>b</sup>	1.01 <sup>a</sup>
	3	59.35 <sup>a</sup>	2.88 <sup>a</sup>	104.67 <sup>a</sup>	3.44 <sup>a</sup>	11.94 <sup>a</sup>	14.16 <sup>ab</sup>	0.96 <sup>a</sup>
2010	1.2	80.90 <sup>a</sup>	3.73 <sup>a</sup>	149.64 <sup>b</sup>	3.41 <sup>b</sup>	13.82 <sup>a</sup>	16.80 <sup>b</sup>	0.92 <sup>ab</sup>
	1.8	85.49 <sup>b</sup>	3.90 <sup>b</sup>	156.76 <sup>c</sup>	3.35 <sup>a</sup>	13.33 <sup>a</sup>	16.17 <sup>ab</sup>	0.91 <sup>ab</sup>
	2.4	78.00 <sup>a</sup>	3.76 <sup>a</sup>	140.33 <sup>a</sup>	3.38 <sup>a</sup>	13.35 <sup>a</sup>	16.59 <sup>ab</sup>	0.89 <sup>a</sup>
	3	85.08 <sup>b</sup>	4.05 <sup>c</sup>	155.00 <sup>bc</sup>	3.33 <sup>a</sup>	13.69 <sup>a</sup>	15.98 <sup>a</sup>	0.95 <sup>b</sup>

Values with the same letters in each column/year are not significantly different at  $\alpha = 5\%$  using Duncan's Multiple range tests.

There were minimal significant effects on boron on pH, Brix, titration acidity and Brix:acid ratios in both the years. There was also very little effect on the color of the samples. If as indicated in the previous section boron was having a positive effect of fruit numbers in all years the likely explanation is that in 2009 the seasons was inadequate to fully take care of the extra fruit at high boron and consequently all fruit were smaller and lower in Brix. Conversely in 2010 the trees could adequately fill all fruit even with a higher fruit set by boron.

Studies conducted by Singh *et al.* (2007) and Wojcik and Levandowski (2003) indicated that boron application did not influence the quality parameters in strawberry but it affected significantly the storage quality attributes of strawberry. Poor accumulation of TSS and Vitamin C content can be the result of B deficiency (Cheng, 1994). However, in the present studies the TSS was in the appropriate range and even the control samples were not boron deficient (Table 4.7). There were no storage experiments done on the treated apricots to determine whether the same sort of negative effects on storage apricots arose from low boron concentrations. These would be worth pursuing in later studies.

#### 4.3.4 Effect of ReTain® on quality attributes of Rival, Goldrich and Orangered® Bhart cultivars of apricots

The effects of AVG were analysed for physico-chemical characteristics. The fresh fruit weight, kernel weight, volume, pH, brix, acidity, color and firmness were measured for two years to enhance understanding of the effects of ReTain® on three varieties of apricots. The varieties were ranked from 1 to 4 depending on the intensity of color through visual color analysis.

**Table 4.4 Mean values of physico-chemical parameters of apricots treated with four different ReTain® treatments, 2009/10 across four boron levels (treatment n=42)**

YEAR	ReTain® Kg/ha	Fruit Fresh Weight (g)	Kernel Weight (g)	Volume (cm <sup>3</sup> )	pH	Brix (%)	Titration acidity (g/L)	Brix:acid ratio
2009	0.00	63.59 <sup>b</sup>	2.91 <sup>a</sup>	117.76 <sup>c</sup>	3.50 <sup>b</sup>	11.58 <sup>a</sup>	14.90 <sup>b</sup>	0.92 <sup>a</sup>
	0.40	63.83 <sup>b</sup>	3.28 <sup>b</sup>	116.23 <sup>c</sup>	3.39 <sup>a</sup>	13.37 <sup>c</sup>	13.69 <sup>a</sup>	1.13 <sup>b</sup>
	0.65	61.91 <sup>b</sup>	3.15 <sup>b</sup>	107.19 <sup>b</sup>	3.41 <sup>a</sup>	12.39 <sup>b</sup>	13.20 <sup>a</sup>	1.07 <sup>b</sup>
	1.00	56.20 <sup>a</sup>	2.91 <sup>a</sup>	94.20 <sup>a</sup>	3.39 <sup>a</sup>	13.01 <sup>b</sup>	13.05 <sup>a</sup>	1.07 <sup>b</sup>
2010	0.00	85.12 <sup>b</sup>	3.91 <sup>b</sup>	157.47 <sup>b</sup>	3.35 <sup>b</sup>	13.57 <sup>a</sup>	16.85 <sup>b</sup>	0.91 <sup>b</sup>
	0.40	86.27 <sup>b</sup>	4.13 <sup>c</sup>	157.59 <sup>b</sup>	3.37 <sup>b</sup>	13.33 <sup>a</sup>	15.69 <sup>a</sup>	0.93 <sup>bc</sup>
	0.65	77.62 <sup>a</sup>	3.87 <sup>b</sup>	144.36 <sup>a</sup>	3.29 <sup>a</sup>	13.48 <sup>a</sup>	17.05 <sup>b</sup>	0.86 <sup>a</sup>
	1.00	80.46 <sup>a</sup>	3.52 <sup>a</sup>	142.32 <sup>a</sup>	3.39 <sup>b</sup>	13.80 <sup>a</sup>	15.95 <sup>a</sup>	0.97 <sup>c</sup>
Values with the same letters in each column/year are not significantly different at $\alpha = 5\%$ using Duncan's Multiple range tests.								

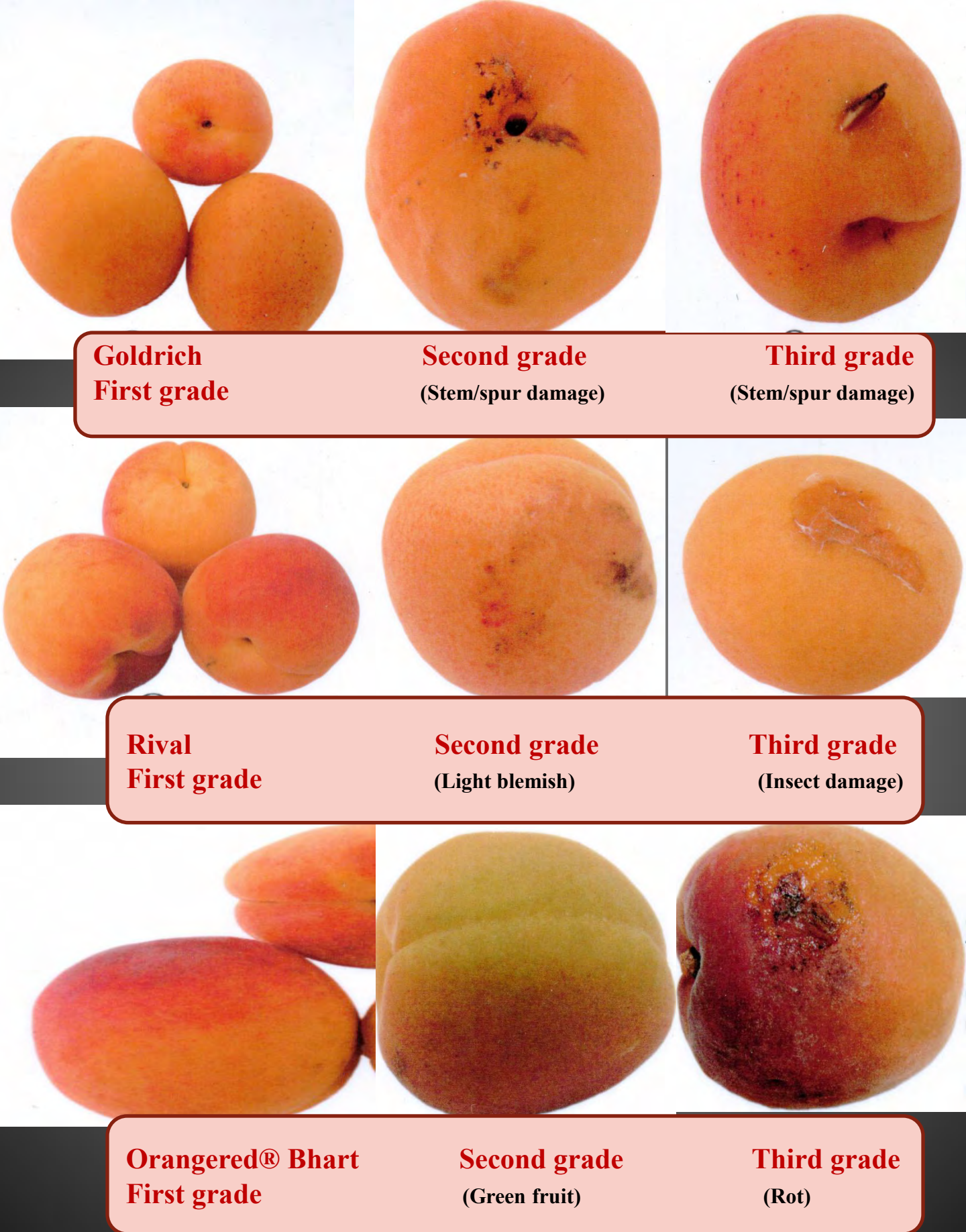
Foliar ReTain® application caused a 2-10% reduction in fresh weight of the apricots in all three varieties for both the years. AVG increased the TSS by up to 15% in 2009. However, the results for 2010 indicated no significant change in TSS (Table 4.4). ReTain® also increased the color of all three varieties in both the years. 1 was coded as light orange, 2 for dark orange, 3 for darkest orange with red tinge and 4 with dark orange with red blush on the apricot. The results for the three varieties and codes for visual color analysis are given in Figure 4.5 a-c. The results are displayed in Table 4.5.



**Table 4.5 Effect of boron and ReTain® on color attribute of three varieties of apricots (Year 2009-2010)**

		Goldrich		Rival		Orangered® Bhart	
		Harvest years		Harvest years		Harvest years	
		2009	2010	2009	2010	2009	2010
<b>Boron</b> <b>Kg/ha</b>	<b>1.2</b>	1.38a	2.00a	2.38b	2.69b	3.38b	3.56a
	<b>1.8</b>	1.31a	1.94a	2.06ab	2.38b	3.19ab	3.31a
	<b>2.4</b>	1.25a	1.81a	1.88ab	2.13ab	3.00ab	3.19a
	<b>3</b>	1.19a	2.00a	1.63a	1.75a	2.69a	3.06a
<b>ReTain®</b> <b>Kg/ha</b>	<b>0.00</b>	1.13a	1.06a	1.56a	1.69a	2.75a	2.88a
	<b>0.40</b>	1.19a	1.94b	1.63a	1.75a	2.69a	2.88a
	<b>0.65</b>	1.38a	1.81b	3.19b	2.69b	3.44b	3.56b
	<b>1.00</b>	1.44a	2.94c	1.56a	2.81b	3.38b	3.81b
<p><i>Values with the same letters in each row/year are not significantly different at <math>\alpha = 5\%</math></i></p> <p><i>The codes for Visual color analysis are listed in Figure 4.6 a-c.</i></p> <p><i>n= 48 for each concentration of boron and ReTain®</i></p>							

The intensity of color decreases with the increase in boron concentration for both the years. The results were consistent for both the season for boron and ReTain® treatments. ReTain® have significant effects on color of apricots. The color of all three varieties have increased with ReTain® treatments. Though Orangered® Bhart itself is an intensely colored variety, there were significant effects of ReTain® on color of Rival and Goldrich variety.



**Figure 4.5** Color diagrams of different grades Rival, Goldrich and Orangered® Bhart apricots



Figure 4.5 a Color development in apricots

Figure 4.b  
Visual color  
analysis



Sample 1



Sample 2

Color code

- |   |          |
|---|----------|
| 1 | Sample 1 |
| 2 | Sample 2 |
| 3 | Sample 3 |
| 4 | Sample 4 |

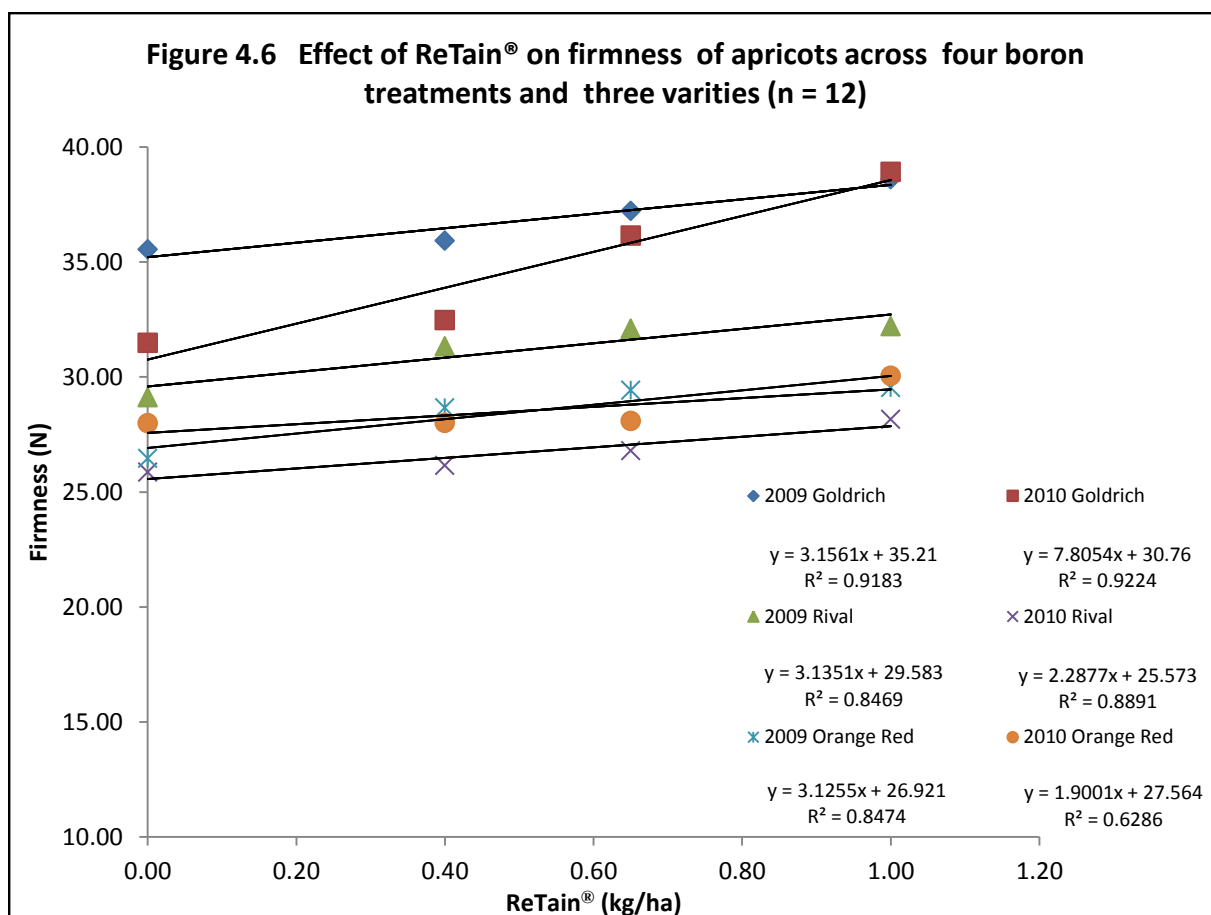


Sample 3



Sample 4





In both years fruits from the trees sprayed with ReTain® had significantly higher firmness of the fruit than those from the control plots. The results are similar to those of Southwick *et al.* (2006) where ReTain® had no effect on the fruit acidity and brix of apricots but had a distinctive effect on firmness of the fruit.

**Table 4.6 Mean values of firmness of three cultivars of apricot treated with ReTain® (Year 2009-2010) across four boron treatments**

ReTain® Kg/ha	Goldrich		Rival		Orangered® Bhart	
	Harvest years		Harvest years		Harvest years	
	2009	2010	2009	2010	2009	2010
0.00	35.55 <sup>a</sup>	31.49 <sup>a</sup>	29.12 <sup>a</sup>	25.86 <sup>a</sup>	26.46 <sup>a</sup>	28.00 <sup>a</sup>
0.40	35.93 <sup>a</sup>	32.48 <sup>a</sup>	31.33 <sup>b</sup>	26.16 <sup>b</sup>	28.66 <sup>b</sup>	28.01 <sup>bc</sup>
0.65	37.22 <sup>b</sup>	36.15 <sup>bc</sup>	32.10 <sup>b</sup>	26.80 <sup>bc</sup>	29.43 <sup>b</sup>	28.09 <sup>bc</sup>
1.00	38.61 <sup>c</sup>	38.92 <sup>c</sup>	32.21 <sup>b</sup>	28.16 <sup>c</sup>	29.54 <sup>b</sup>	30.05 <sup>c</sup>

Values with the same letters in each column are not significantly different at  $\alpha = 5\%$ .  
Means separation within columns by Duncan's Multiple range tests.  
Mean values of 12 samples for individual treatment.

The R3 treatment of ReTain® (0.65kg/ha) improved the firmness of Rival variety from 2-10 % , Goldrich from 8 -23% and Orangered® Bhart from 7.3-11.6% compared to the control sample (Table 4.6). The effect was most prominent in the Goldrich variety for both the seasons. For Rival and Goldrich the average firmness in 2010 was less than in 2009. Figure 4.6 indicates the increase in firmness in all three varieties for both the seasons due to the effect of ReTain®. With increase in concentration of ReTain® the firmness of the sample increases with no change in Brix and TSS as indicated in Table 4.4. The fresh weight of the ReTain® treated fruits decreased and this result is similar to the results of Bregoli *et al.* (2002).

Table 4.6 reveals the mean values of 12 samples analysed for fresh fruit firmness for the individual treatments for both the seasons. The highest concentration of ReTain® had maximum firmness for all three varieties. Goldrich was the firmest variety followed by Rival and Orangered® Bhart.

#### 4.3.5 Boron nutrient content in three apricot cultivars

The concentration of B across a range of different times after sprays at different concentrations sprays in leaves, branches and fruits was measured with ICP-OES to study the uptake of B by different plant parts. The Mean values of B status in different plant parts is listed in Table 4.7. The adequate boron level for apricot is 20-60 ppm in leaves (Reuter & Robinson, 1986).

It can be seen that the higher levels of B application lead to increased levels of B in leaves, branches and fruits. Using normalised values for each treatment variety ( $\text{variety} \times \text{value} / \text{mean} \times \text{variety} \times \text{value}$ ) allowed a regression of leaves, branches and fruits against treatment number. Slopes were 4.4%, 3.0% and 4.1% with adjusted R<sup>2</sup> values of 0.57, 0.34 and 0.39 and significant P values of 0.003, 0.028 and 0.018 for leaves, branches and fruits respectively.

These indicate that foliar sprays with boron significantly increased tree content. The three varieties had different levels of boron in their organs. Rival had a higher level in the leaves than Goldrich but a lower level in the branches. The maximum increase in boron mineral content was observed in leaves of Rival by up to 19% compared to the control, followed by Orangered® Bhart by up to 11% and Goldrich by up to 5 %.

The boron concentration in fruit have distinct differences among the three varieties. The boron nutrient status of Rival fruit showed the greatest increased by up to 11%. However, Goldrich had the highest value for boron in the fruit.

**Table 4.7 Boron content (mg/Kg) in leaves, branches, and fruit averaged across four collection times at different developmental stages after each boron spray.**

	Boron treatments	Rival	Goldrich	Orangered® Bhart
<b>Leaves</b>	B0	42.43	35.65	31.30
	B1	44.58	37.63	33.77
	B2	44.48	37.78	32.27
	B3	53.33	38.45	36.07
<b>Branch</b>	B0	23.20	26.00	19.43
	B1	21.80	23.05	20.47
	B2	23.53	27.75	20.20
	B3	25.13	27.25	21.23
<b>Fruit</b>	B0	42.75	54.25	33.07
	B1	42.33	47.98	35.57
	B2	43.65	61.93	35.57
	B3	47.55	62.83	35.20

*Treatment concentration listed in Table 3.4*

*Values are the means of four sprays performed at different developmental stages as listed in Table 3.4.*

For branches the increasing concentration of B sprays increased the B status in branches by up to ~8-9 % in Rival and Orangered® Bhart and 6 % in Goldrich. Thus the foliar spray were effectively absorbed by all plants in the trial. Overall, except for some branch values there seemed to be adequate amounts of boron in the fruit and vegetative parts of the trees whether higher levels of b were sprayed or not. Thus it is a little surprising that the earlier figures and tables have indicated so many significant effects of the boron treatments. These data thus suggest the deficient level for boron may be higher than the published value of 20ppm (Reuter & Robinson, 1986).

The Brix value in Rival was the highest and this could arise from interactions with the effect of available B in fruit and branches. The percent of soluble solids (mostly sugars) in cantaloupe fruits was increased from around 8% to 10% by foliar application of B (Stark and Matthews, 1950).

The B concentrations in leaves, branches and fruits increased with the respective increased application rates of boron indicating that boron when applied

through foliar means is readily available to plants and then translocated to different parts where B is involved in several vital processes and affect many pathological and physiological disorders (Conway *et al.*, 1992; Fallahi *et al.*, 1997; Hernandez-munoz *et al.*, 2006).

#### 4.3.6 Physico-Chemical parameters of three cultivars of apricot

Table 4.8 Mean values of physico-chemical parameters of three cultivars of apricot, 2009/10 across all boron and ReTain® treatments.								
YEAR	Cultivar	Fruit Fresh Weight (g)	Kernel Weight (g)	Volume (cm <sup>3</sup> )	pH	Brix (%)	Titration acidity (g/L)	Brix:acid ratio
2009	Rival	71.43 <sup>c</sup>	3.11 <sup>b</sup>	123.85 <sup>b</sup>	3.60 <sup>c</sup>	14.62 <sup>c</sup>	10.49 <sup>a</sup>	1.47 <sup>c</sup>
	Goldrich	51.32 <sup>a</sup>	3.07 <sup>b</sup>	92.36 <sup>a</sup>	3.20 <sup>a</sup>	11.47 <sup>b</sup>	16.14 <sup>b</sup>	0.73 <sup>a</sup>
	Orangered® Bhart	63.60 <sup>b</sup>	2.85 <sup>a</sup>	119.23 <sup>b</sup>	3.4 <sup>b</sup>	10.68 <sup>a</sup>	15.68 <sup>b</sup>	0.81 <sup>b</sup>
2010	Rival	87.65 <sup>b</sup>	3.38 <sup>b</sup>	154.95 <sup>b</sup>	3.39 <sup>b</sup>	13.91 <sup>b</sup>	17.28 <sup>b</sup>	0.82 <sup>b</sup>
	Goldrich	100.66 <sup>c</sup>	4.95 <sup>c</sup>	188.14 <sup>c</sup>	3.07 <sup>a</sup>	12.27 <sup>a</sup>	20.74 <sup>c</sup>	0.60 <sup>a</sup>
	Orangered® Bhart	58.79 <sup>a</sup>	3.24 <sup>a</sup>	108.21 <sup>a</sup>	3.58 <sup>c</sup>	14.46 <sup>c</sup>	11.13 <sup>a</sup>	1.33 <sup>c</sup>
<p>Values with the same letters in each row/year are not significantly different at <math>\alpha = 5\%</math>  Means separation within columns by Duncan's Multiple range test, <math>P \leq 0.05\%</math>  Mean values of 192 samples for each variety</p>								

Table 4.8 gives the results for all three cultivars across two years. It can be seen that the agreement from year to year was quite variable. For example the fresh weight of Goldrich was the lowest in 2009 compared to other varieties and the highest in 2010. Overall for the 21 comparisons only in 4 did the relative ranking of a variety remain consistent from one year to the next. The critical issue however is that the varieties and years did provide a wide range of different environments in which to compare the effects of boron and ReTain®. In both years there were significant effects of variety for all seven characters.

Table 4.9 gives the full range of significance values for the main effects and interaction effects of the complete significance analysis. Significant differences existed in the way the varieties behaved for all but one quality attribute across the two years. Variety had few significant interactions in 2009 but had significant interactions for nearly all characteristics with both ReTain® and boron in 2010.

**Table 4.9 Significance values for the GLM model for all physico-chemical parameters of apricots for two years, 2009/10**

YEAR	Treatment	Fresh Weight (g)	Kernel Weight (g)	Volume (cm <sup>3</sup> )	pH	Brix (%)	Titration acidity (g/L)	Brix: acid ratio
2009	Variety	0.001*	NS	0.001*	0.001*	0.001*	0.001*	0.001
	ReTain®	0.001*	0.001*	0.001*	NS	0.01*	NS	NS
	Boron	NS	NS	0.001*	NS	0.31*	0.045*	NS
	Variety * ReTain®	NS	NS	NS	NS	0.001*	NS	0.001*
	Variety * Boron	0.027*	NS	0.002*	NS	NS	NS	NS
	ReTain® * Boron	0.001*	0.003*	S*	0.008*	NS	0.001*	0.001*
	Variety * ReTain® * Boron	0.002*	0.001*	0.001*	0.019*	0.001*	0.026*	0.001*
2010	Variety	0.001*	0.001*	0.001*	0.001*	0.001*	0.001*	0.001*
	ReTain®	0.001*	0.001*	0.001*	0.001*	NS	0.001*	0.001*
	Boron	0.001*	0.001*	0.001*	0.001*	0.044*	0.004*	0.021*
	Variety * ReTain®	0.048*	0.001*	0.001*	0.001*	0.001*	0.001*	0.001*
	Variety * Boron	0.006*	0.001*	0.001*	0.001*	NS	0.001*	0.001*
	ReTain® * Boron	0.001*	0.00*	0.001*	0.001*	0.001*	0.007*	0.003*
	Variety * ReTain® * Boron	0.001*	0.001*	0.001*	0.001*	NS	0.001*	0.001*
<i>p values of Tukey; S* : significant ≥ 99.9%; NS: not significant &lt; 95%; (192 samples)</i>								

ReTain® had more significant effects than boron though both treatments affected most characteristics in 2010. ReTain® and boron had significant interactions for most characters in both years.

Taken as a whole the trial produced numerous significant results for treatments with ReTain® and boron within a wide set of environments. However, many of the effects were complicated by interactions with variety and each other (ReTain® and boron) and differed from year to year. This indicated considerable care would need to be taken in introducing new agronomic treatments in the production of apricots as quality could easily be affected in a variable manner.



#### 4.3.7 Discussion

In this experiment, four foliar sprays of boron and four levels of foliar sprays of ReTain® application were investigated as a foliar spray program to increase fruit firmness and fruit yield. The firmness criteria was of specific concern as the local Tasmanian orchards have soft apricots and the export of fruit within the limited time span of apricot shelf life is an issue. The present spray program has reduced the issue to some extent for certain varieties of apricots. As a result of these findings The Qew Orchard is now using ReTain® on a few varieties of apricots to delay the ripening period of the fruit and increase the firmness attributes. However, further research on volatile profiles, sensory analysis and consumer perception for individual treatments will enhance our understanding of the use and value of a boron/ ReTain® spray program.

The foliar application of boron increased fruit yield and fruit set in the present study. Johnson *et al.* (1955) and Woodbridge *et al.* (1952) also revealed that in pear, foliar B applications were more effective in increasing fruit yield than supplying pears with B via the soil. The higher tree productivity in the foliar B treatments may have been caused by the increase of B concentration in the flowers which led to an increased fruit set.

It would appear that increases in the concentrations of sugars in fruit of plants supplied with supplemental boron must be the result of an increase in translocation of sugar rather than an effect on photosynthesis since the leaves of boron deficient plants are consistently abnormally high in sugars. In the woody Rosaceae (apples, pears, stonefruit), the sugar alcohol sorbitol is the major photosynthetic product at 60–85% of transported carbon, the remainder being mainly sucrose. Regardless of transport form, photoassimilate arriving in fruits is rapidly converted to the storage products characteristic of the fruit in question (principally starch, glucose, fructose and sucrose). Thus the identity of labelled sugars in fruits often differs markedly from the form transported.

The studies of Gauch & Duggar (1953) suggests that boron binds with sugar to form a sugar borate complex which moves through cellular membranes more readily than non borated sugar molecules. However, in our study there was not a consistent increase in Brix for fruit with higher B applications nor were the highest B containing varieties necessarily highest in Brix. Thus sugar translocation for storage in the fruit did not seem to be the mode of action of B on fruit set.

It is possible to breed new cultivars which set and retain optimum numbers of fruits consistently from season to season. It could be achieved by production of cultivars which are parthenocarpic or self fertile, or which have late flowering time, frost resistant or which have very long effective pollination periods. Under these circumstances use of B to increase fruit set would be unnecessary. Thus use of B in the orchard may be variety specific.

Fruit size is one of the external quality characteristics having the greatest influences on the commercial value of apricot fruit. The increase in total fruit set due to the effect of foliar boron application had no effect on fruit size of the Rival, Goldrich and Orangered® Bhart variety. However there was reduction in fruit size when a combination of ReTain® and boron was used. These results were similar to the studies of peaches, where fresh weight and dry weight of fruits treated with AVG were significantly lowered than the control. (Bregoli *et al.*, 2002). The results were contradictory to Ju *et al.* (1999), where ReTain® applied two weeks before commercial harvest of “Feicheng” peaches increased fruit size. The size was significantly greater on AVG treated trees compared with the controls when fruit set was controlled to the same level by hand thinning.

Fruit softening in peaches is correlated with an increase in ACC and ethylene production (Tonutti *et al.*, 1996; 1997). AVG applied as a pre-harvest spray to peaches delays maturation (Belding and Lokaj, 2002; Ju *et al.*, 1999; McGlasson *et al.*, 2005). There are contrasting results on apple and peach fruits. The effects of ReTain® also depending on the cultivar and on the timing of the foliar spray treatment.

For Oregon Spur apples, William (1980) did not observe any differences in flesh firmness between treated and untreated fruit before and at harvest. The same results were observed in the study of Puritan apple fruits (Autio and Branlage, 1982) where ReTain® had no effect on TA, SSC and flesh firmness. However, flesh firmness was higher in AVG treated Golden delicious apples (Bangerth, 1978). AVG-treated Redhaven peaches exhibited significantly higher flesh firmness (Bregoli *et al.*, 2002).

AVG has been reported to delay color development in apple cultivars of Gala and Jonagold (Wang and Dilley, 2001), McIntosh (Stover *et al.*, 2003), Gala and Cripps Pink (Phan-thien *et al.*, 2004). Ethylene biosynthesis during maturation and ripening appeared to play an important role in the development of color and

anthocyanin accumulation in AVG treated fruit. AVG might delay or inhibit the expression of anthocyanin biosynthetic genes (Awad and de Jager, 2002). The leaves (Fruetel and Soest, 1997) readily absorb AVG and this may lead to the suppression of fruit ripening through several mechanisms.

It had been believed that the efficacy of AVG in climacteric fruit was a consequence of uptake through the peel to directly inhibit ACC synthase in the fruit. However, more recent studies have indicated that the effect caused by exposure of the abscission zone (AZ) to AVG, translocation of AVG (or a metabolite) from the leaves or branches to the fruit, or modification of the leaf fruit signalling linked to the onset of fruit ripening are three other possible mechanisms (Rath *et al.*, 2006).

Fruit softening in peaches is correlated with an increase in ACC and ethylene production (Tonutti *et al.*, 1996; 1997). AVG applied as a pre-harvest spray to peaches delays maturation (Belding and Lokaj 2002; Ju *et al.*, 1999; McGlasson *et al.*, 2005) and post-harvest dips slow the softening of various cultivars of peaches and nectarines (Byers 1997; Garner *et al.*, 2001). AVG had very similar effects seen in peaches in the present studies where the firmness of the apricots increased with increasing concentration of applied ReTain®.

#### 4.3.8 Conclusion

Farmers have historically increased the fruit size by hand thinning the fruits. The boron treatments accelerated fruit growth and decreased fruit drop with minimum effect on fruit size allowing for more fruits per tree and increasing yield. Therefore an alternative method to hand thinning may be use of a pre harvest foliar B spray program which can maximize fruit set with minimal effect on fruit size in Rival, Orangered® Bhart and Goldrich apricots. This, along with the relatively high levels of B found in the untreated trees, suggests that flowering and fruit set may have a greater demand for B than does vegetative growth.

Experimental field trials need to be carried out on other varieties of apricots to understand the effects of foliar boron spray in general for apricots. All three varieties behaved differently to B application and the results of both the years were not sufficiently consistent to give general conclusions at this stage.

Organic and inorganic metabolites are translocated from leaves to fruit buds (floral buds), woody parts and roots of plants during senescence (Nooden, 1986). B has a special role in remobilization (Brown and Hu, 1996).

From the present studies, it is evident that foliar application of boron had significant effects on flower buds, fruit drop and fruit yield but no effects on physico-chemical parameters of the Rival, Goldrich and Orangered® Bhart varieties of apricots.

ReTain® dominated the effects of boron for most of the quality parameters. AVG application improved firmness of the fruits in all three varieties. There were no significant effects of boron on Brix, TA, firmness and color attributes of Rival, Goldrich and Orangered® Bhart. The prefoliar sprays of boron improved the fruit set and thereby fruit yield and the combined sprays of ReTain® and boron improved firmness of the samples with no effect on sugars and acidity of the fruit.

A detail analysis of the aromatic profile along with the careful determination of its odor contribution will provide useful indications of overall fruit quality and treatment effects.

## CHAPTER 5 EFFECT OF BORON AND ReTain® ON VOLATILE COMPONENTS OF THREE VARIETIES OF APRICOT

### Abstract

Aroma compounds are present in raw foods either as free compounds or glycosidically bound (aroma precursors). The differences in volatile constituents due to the boron and ReTain® treatment effects were investigated by means of HS-SPME (Head Space, Solid Phase Micro Extraction) using Carboxen-Polydimethylsiloxane fibers. The free aroma compounds were identified by Gas Chromatography and Mass Spectroscopy (GC-MS), common compounds such linalool,  $\alpha$ -terpineol,  $\beta$ -ionone,  $\gamma$ -decalactone as well as 26 other compounds were found. The volatiles are divided into five groups; esters, lactones, ketones, carbonyl compounds and terpenic compounds. Fenchone was used as internal standard. The three varieties of apricots produced different concentrations of the volatiles. The total volatile constituents extracted with HS-SPME were greatest for Rival and least for Goldrich. The Multivariate analysis showed a significant combined treatment effect of boron and ReTain® on the terpenes released for all three varieties. The amount of esters, lactones and terpenic acids released were more than carbonyl compounds. Though more than 50 compounds were found with SPME thirty identified volatiles were measured in the process.

### 5.1 Introduction

The aroma of apricot is one of the most significant and decisive parameters of quality in the selection of a product. Aroma compounds are present in raw foods in free volatile form and as non-volatile precursors such as substituted cystein sulfoxides, thioglycosides, glycosides, carotenoids and cinnamic acid derivatives (Crouzet *et al.*, 1995). The formation of the volatile compounds in fruits is a dynamic process, and generally the typical flavor of most of them is not present at harvest but develops after a ripening process. In contrast to other fruits such as apple and peach the flavor of apricot, although strong and typical, has hardly been investigated.

Apricot fruits are appreciated by the consumers for their flavor, sweetness and juiciness, characters strongly related to the variety and ripening stage at harvest (Botondi *et al.*, 2003). The variability of aroma compounds has been reported to depend on cultivars (Souty, 1988; Marcus *et al.*, 1989), maturity or processing and storage conditions. Typically the formation of volatile flavor compounds occurs during the latter stages of the ripening process when the enzymes, which catalyze the formation of the flavor compounds, become active (Perez *et al.*, 1996)

Solid phase micro extraction (SPME) was the technique that provided resolution of the highest number of aromatic compounds, which determine the characteristic aromas of the apricot fruit. Ideally, the methods used for flavor analyses should not only avoid changes in the natural flavor pattern, but like SPME should be fast, solvent-less, amenable to automation, and inexpensive. The aroma of a food is not related to the total concentration of volatile compounds, but to the levels of the various aromatic compounds which are characteristics of the fruit that are in that volatile fraction (Solis-Solis *et al.*, 2007).

Many factors affect the reproducibility and sensitivity of SPME during analysis of headspace volatiles, including type and size of the solid phase, ratio of liquid to headspace volume, isolation duration, isolation temperature, and characteristic of the liquid matrix (Penton, 1999). Though we found many peaks overlapped or were incompletely separated at certain concentrations, the dilution of apricot extract was effective in resolving most of the important components. The main drawback of this technique is relatively high cost of fibre and a limited duration of use of fiber associated with the pollution during the extractions and eventually degradation. Sometimes additional peaks are found in chromatograms due to desorption at high temperature and matrix effects may impair the accuracy and precision of the analysis (Penton , 1999).

In spite of the importance for fruit quality the evolution of apricot volatiles due to the effects of pre harvest treatments has, to our knowledge not been extensively studied. The main aim of the present study was (1) to investigate the changes in volatile constituents of 3 apricot cultivars and (2) to compare the effects on the levels of volatiles of these 3 cultivars due to the preharvest foliar sprays of boron and ReTain®.

## **5.2 Materials and methods**

This chapter evaluates the main effects and interaction effects in a complete factorial design of the treatments on volatile components of apricots after harvest. Table 5.1 outlines the main treatments and measurement evaluated. The complete details are described in subsequent tables and figures.

**Table 5.1. Design of different foliar treatments and evaluated measurement for volatiles**

	Selection of 3 apricot varieties	Foliar Treatments		Qualitative analysis	
		Boron	ReTain®	Volatile Groups	Individual volatiles
Numbers	3	4	4	5	30
	2 middle harvest (Rival, Goldrich) 1 early harvest (Orangered® Bhart)	1.2 Kg B/ha - 3 Kg B/ha	0–1 Kg/ha	Esters (0.02 ppm –13.42 ppm) Aldehydes/lactones (0.01 ppm – 4.11 ppm) Ketones (0.00 ppm – 15.90) Carbonyl compounds (0.02 – 195.55 ppm) Terpenes/Terpene alcohols (0 -98.45 ppm)	Mentioned in detail In Table 5.4 to Table 5.10
Concentrations expressed relative to internal standard 0.1 mg fenchone.					

The volatile fraction of three different varieties of apricot namely Rival, Goldrich and Orangered® Bhart was analysed by headspace solid phase microextraction (HS-SPME) followed by gas chromatography mass spectroscopy (GC-MS) as discussed in 3.1.6. Sample preparation, GC set up and methodology including trial layout and application rates are found in 3.1.6.2 and 3.1.6.3. Sample components were identified by comparison of the compound's Kovats index, *I* (Kovats, 1958), and mass spectrum with that of an authentic reference standard.

The concentration of volatile compounds was determined in parts per million and calculated from the sum of total area of all compounds assuming a response factor of unity. Values are expressed in parts per million (ppm) equivalents of fenchone. Prior to use, all fibers were conditioned following the manufacturer's recommendations. Each day, before the sample analyses started, a short thermal cleaning of the fibers in a GC injector (30 min at 250 °C) and a blank run were performed.

The analysis of the volatile fraction consists of a number of complementary steps: separation, identification, quantitative determination of components and further data processing to increase the amount of information provided by the analysis. The analysis of volatiles is based on the extended concept of dimension involving all steps of the analytical process, which are sample preparation, separation, detection and data elaboration.

With SPME nearly 50 compounds were separated from which 30 were identified. Among the volatiles characterized in the whole fruit samples of the three varieties, six major volatile compounds were identified that belonged to the alcohols, aldehydes, esters, ketones and terpenes chemical groups. The conditions of SPME for the reproducible and

accurate analysis of headspace volatile compounds in apricots were optimized by conducting different trials.

The selection of the internal standard for the SPME technique is usually to use a compound absent in the fruit. As shown by previous studies of the aroma potential of apricots, many of the compounds used in trials of other fruits as internal standards were already present in the apricots and thus not useable. As fenchone was accessible in the laboratory and present in extremely low amounts in apricot fruits, it was used as an internal standard at 0.949 µg/ml.

The concentration of volatile compounds was determined in parts per million of pulp for all techniques. The concentration was determined from the sum of the total area of all compounds detected by GC-FID. The compounds included all the free volatile compounds (VC) including aroma compounds (AC). The volatiles are divided into five group esters, lactones, ketones, carbonyl compounds and terpenic compounds.

No previous studies have investigated the effect of boron, ReTain® or a combination of boron and ReTain® on volatiles in different varieties of apricots. The present study is therefore the first study to show the effects of (the plant growth regulator) ReTain® and boron as well as their combination on volatile constituents for three different varieties of apricots. This chapter is divided into four parts to discuss the results in detail.

5.3 Overall effects of all treatments on volatile constituents of three varieties of apricots.

5.4 Individual effects of boron on volatile constituents of three varieties of apricots.

5.5 Individual effects of ReTain® on volatile constituents of three varieties of apricots.

5.6 Combined effects of boron and ReTain® on volatile constituents of three varieties of apricots.

### **5.2.1 Statistical analysis**

Results for total peak areas and selected volatile peak areas were statistically analysed by multivariate analysis and Duncan's multiple range test using the commercially available software package SPSS software program (SPSS Inc., Chicago, Ill., U.S.A.). Descriptive statistics including mean, standard deviation, minimum to maximum range of volatiles in ppm and percentages were calculated. A *P*-value < 0.05 was considered significant. Multivariate analysis using Principal Component Analysis (PCA) for the volatiles found by SPME-GC/MS was conducted using statistical software package R (GNU General Public License).



### 5.3 Overall effects of all treatments on volatile constituents of apricots

Table 5.2 shows the relative concentrations of volatile compounds (VC) extracted for three apricot varieties. Though most of the extracted VC were the same the concentrations of the VC were different in all 3 varieties. Rival variety had the highest VC concentration while Goldrich had the lowest. These variety rankings were not related to the maturity period as Orangered® Bhart is a precocious variety and Rival as well as Goldrich are half season varieties.

**Table 5.2 The relative total concentration of volatile constituents extracted for four different boron and ReTain® treatments of three apricot varieties**

Treatments <sup>a</sup>	Goldrich (ppm) <sup>b</sup>	Rival (ppm) <sup>b</sup>	Orangered® Bhart (ppm) <sup>b</sup>
ROB0 (Control)	25.05	132.48	63.48
ROB1	28.76	66.07	76.00
ROB2	28.85	285.03	246.33
ROB3	34.58	149.62	82.41
R1B0	31.44	75.09	76.16
R1B1	26.78	173.70	155.03
R1B2	25.72	165.55	100.06
R1B3	30.16	145.62	164.21
R2B0	24.04	177.70	69.21
R2B1	42.12	201.55	209.07
R2B2	25.04	178.20	127.49
R2B3	19.03	154.36	106.35
R3B0	20.53	103.57	36.71
R3B1	25.27	187.51	86.97
R3B2	19.75	136.14	60.29
R3B3	21.36	99.52	54.97
<b>Mean</b>	26.78	151.98	107.17
CV <sup>c</sup>	22%	35%	55%
<b>Range</b>			
Minimum	19.03	66.07	36.71
Maximum	42.12	285.03	246.33

<sup>a</sup> Concentrations of treatment are represented in Table 5.3 <sup>b</sup> Concentrations expressed relative to internal standard 0.1 mg fenchone. Results are for internal comparisons only. Percent recoveries and FID response factors were not determined for each compound (assumed all response factors = 1). <sup>c</sup> CV = Coefficient of Variation.

**Table 5.3**  
Concentrations of  
Treatments

**Boron**

B0 = 1.2 Kg B/ ha

B1 = 1.8 Kg B/ ha

B2 = 2.4 Kg B/ ha

B3 = 3.0 Kg B/ ha

**ReTain®**

R0 = Water (control)

R1 = 0.40 Kg/ ha

R2 = 0.65 Kg/ ha

R3 = 1.00 Kg/ ha

Table 5.4 lists the apricot headspace constituents isolated with the SPME technique. A GC-FID chromatogram of apricot headspace volatiles is shown in Figure 5.1. A total of 2 esters, 2 aldehydes, 2 lactones, 4 ketones, 7 carbonyl compounds, 17 terpenes and terpene alcohols making a total of 30 components were identified in all extracts of boron and ReTain® treated samples across all three varieties. Structural diagrams of 15 important compounds are given in Figure 5.3.

In all of the 3 varieties, 10 common and important volatile compounds identified in previous studies were found. They were  $\alpha$ -terpineol, with characteristic floral notes, limonene and cymene with its citrus notes,  $\beta$ -ionone resembling cedar wood odour and a raspberry like undertone, myrcene,  $\gamma$ -decalactone with typical peach and apricot jam notes (Guillot *et al.*, 2006), benzaldehyde, geraniol, hexanal with its grassy notes and ocimenol isomers. The odour of high grade  **$\alpha$ -terpineol** is delicately floral and sweet of the Lilac type. It is one of the most commonly used of all perfume chemicals. It's very low cost, excellent availability, general stability in air, soap, solvents and other chemicals and its formulations make it an everyday, all-purpose material in most perfume laboratories and compounding factories.

**Limonene** has fresh, light and sweet citrusy odour with a strong resemblance to orange peel oil. It is colorless and used as perfumery in soaps and detergents. In detergents it is found together with benzyl acetate. The flavor of d-limonene is sweet and refreshing and its odour is mild citrus like and orange like. l-limonene is of synthetic origin and is not found naturally in fruits. d-Limonene is used very extensively in perfume compositions to give a refreshing top note.

**Cymene** is sometimes known as cymol. Less pure commercial grades display typical gassy kerosene like odour, while a highly purified form smells more of citrusy, reminiscent of Lemon and Bergamont top notes, having more freshness.

**$\beta$ -ionone** also known as 4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-one has a warm, woody odour with a fruity undertone. It is used in perfumery and in flavor composition for imitation of berry, grape, nut and fruit complexes, pistachio, pineapple in floral complexes and liqueur flavors.

The odour of **myrcene** is refreshing, almost citrusy, but warm balsamic and ethereal sweet.

**$\gamma$ -decalactone** exists in several isomer forms and three of them are commercially available. It has powerful creamy, fruity, peach like odour and its main use is in flavor compositions.

**Benzaldehyde** probably arises from the cyanogenic glycoside, amygdalin, and a typical constituent of many *Prunus* species such as apricot.

**Geraniol** is a terpene alcohol which possesses a sweet rose type odour. It is extensively used in perfumes from delicate lotion perfumes and soft domestic fragrances, to sweet floral household odours and even in low-cost soap perfumes.

The powerful green grassy odour of **hexanal** can be diluted to be more reminiscent of freshly cut grass and unripe fruit of plum or apple. It is used to mask industrial odour.

The **ocimanol** isomers exist in cis- and trans- form. The compounds were 2, 6-Dimethyl-5, 7-octadien-2-ol and 2,6-Dimethyl-3,5-octadien-2-ol. Ocimanol isomers have diffusive and refreshing camphoraceous lime like odour with an undertone of floral sweetness. It is produced from by hydration of Ocimene and used in floral and green-floral fragrances, modern soap perfumes and cologne fragrance.

There was a huge amount of data to access and analyse from the chromatograms obtained and the total analytical analysis was time consuming beyond that available for the present studies. As a result a preliminary analysis of 30 volatiles was used to describe the main effects for the whole experiment to study the treatment effects. Figure 5.1 shows an example of the chromatogram of apricot volatiles. The 30 isolated volatile compounds along with internal standard (fenchone) obtained with headspace solid phase micro extraction (HS-SPME) can be seen in the chromatogram. As shown in Table 5.2 the total volatile constituents extracted with HS-SPME was greatest for Rival and least for Goldrich. All three varieties of apricots produced different concentrations of the volatiles.

Figure 5.1 HS- SPME GC MS chromatogram of Rival

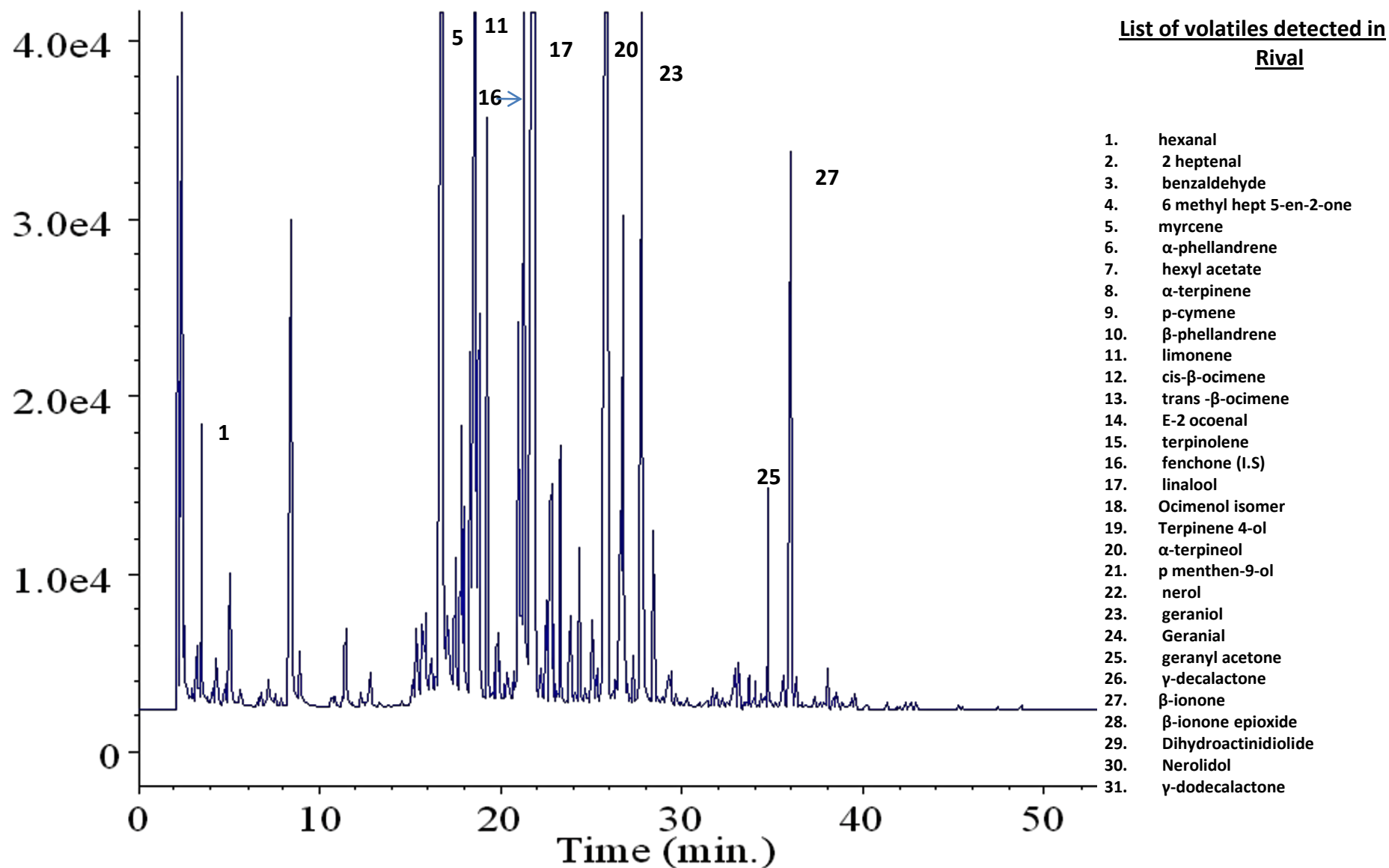
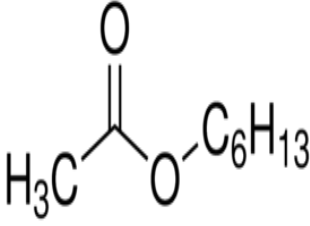
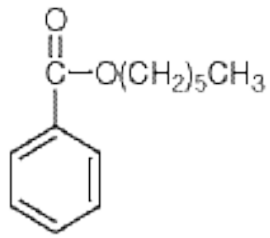
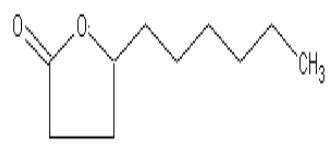
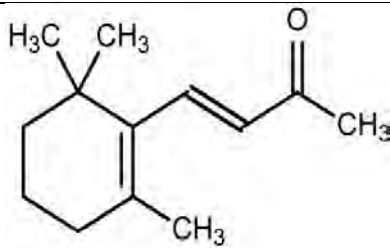
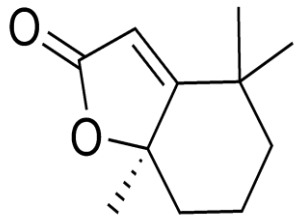
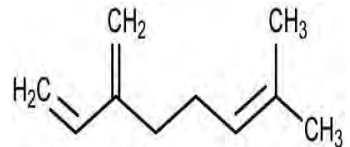
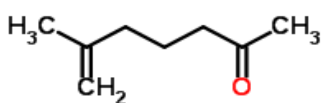
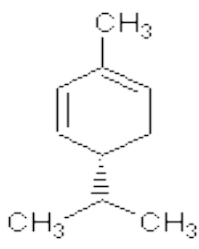
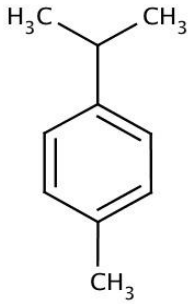
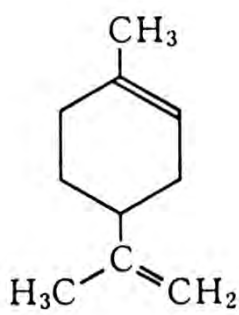
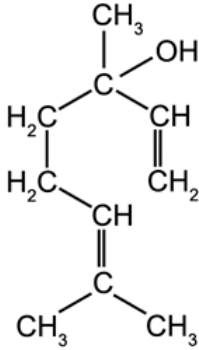
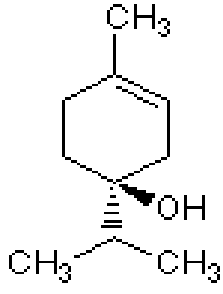
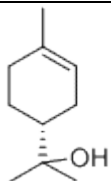
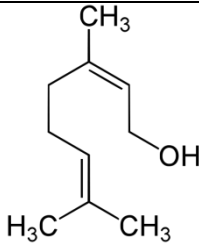
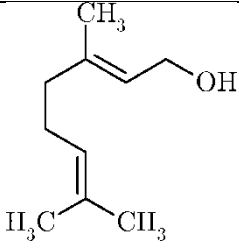
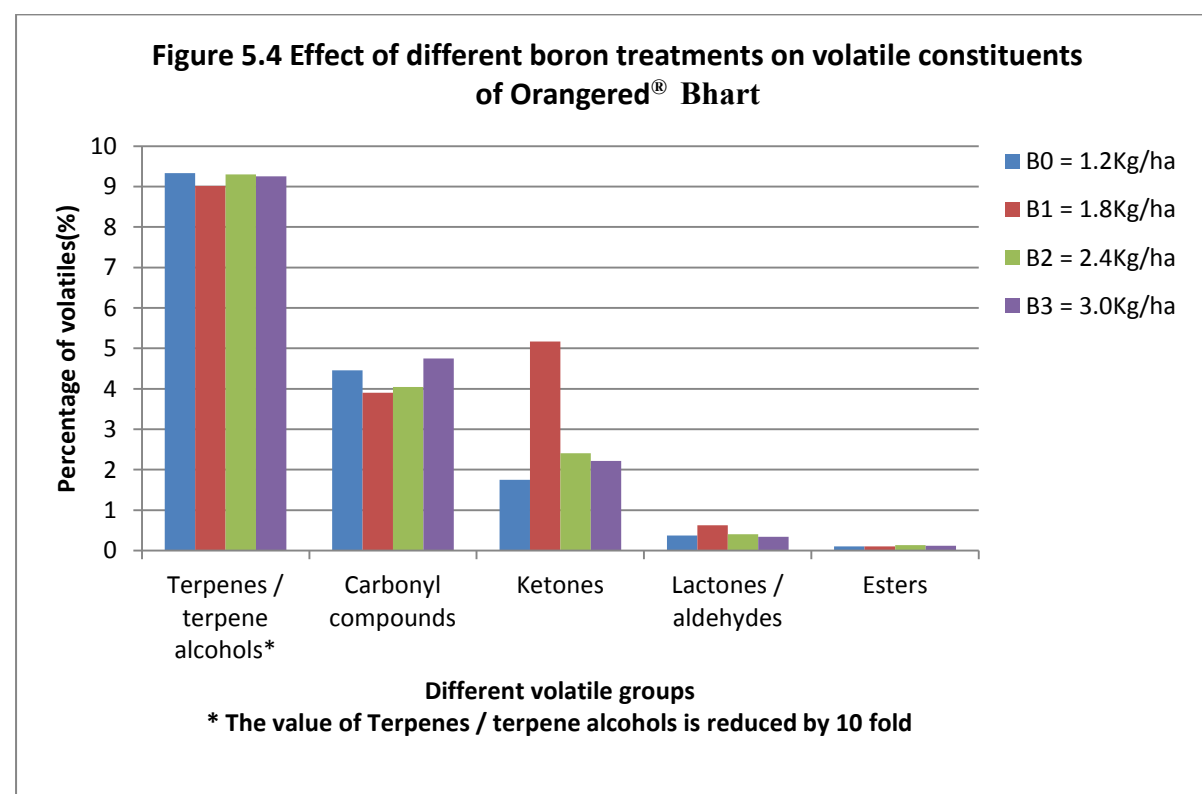
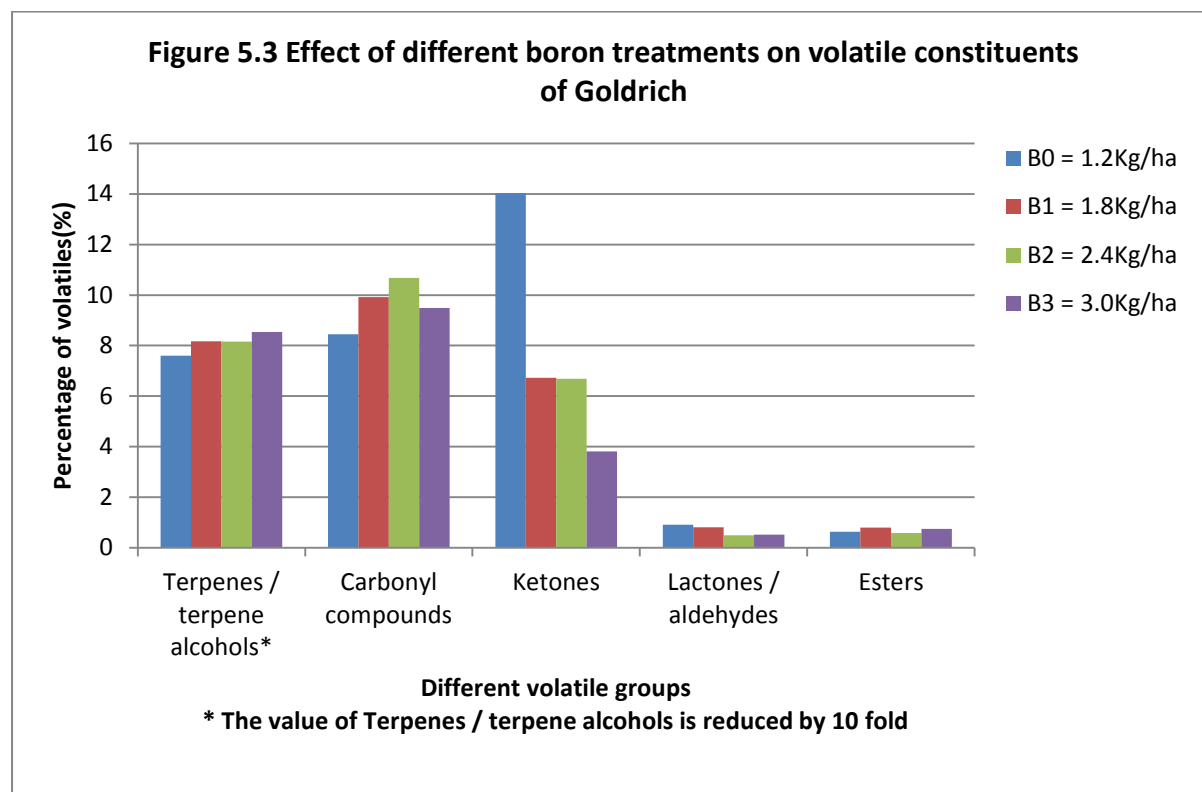


Figure 5.2 Structure diagrams of 12 important volatile compounds of apricot flavor

(Source: Handbook of fruits and vegetables, Hui *et.al.*, 2010)

		
Hexyl Acetate	Hexyl Benzoate	γ-decalactone
		
β-ionone	dihydroactinidiolide	myrcene
		
6-methylhept-5-en-2-one	α-phellandrene	p-cymene
		
Limonene	Linalool	Terpinen-4-ol
		
α-terpineol	Nerol	Geraniol

## 5.4 Individual effects of boron on volatile constituents of three varieties of apricots



**Table 5.4** Minimum and maximum range and mean values of volatile compounds of three different apricot cultivars treated with four levels of boron and ReTain®

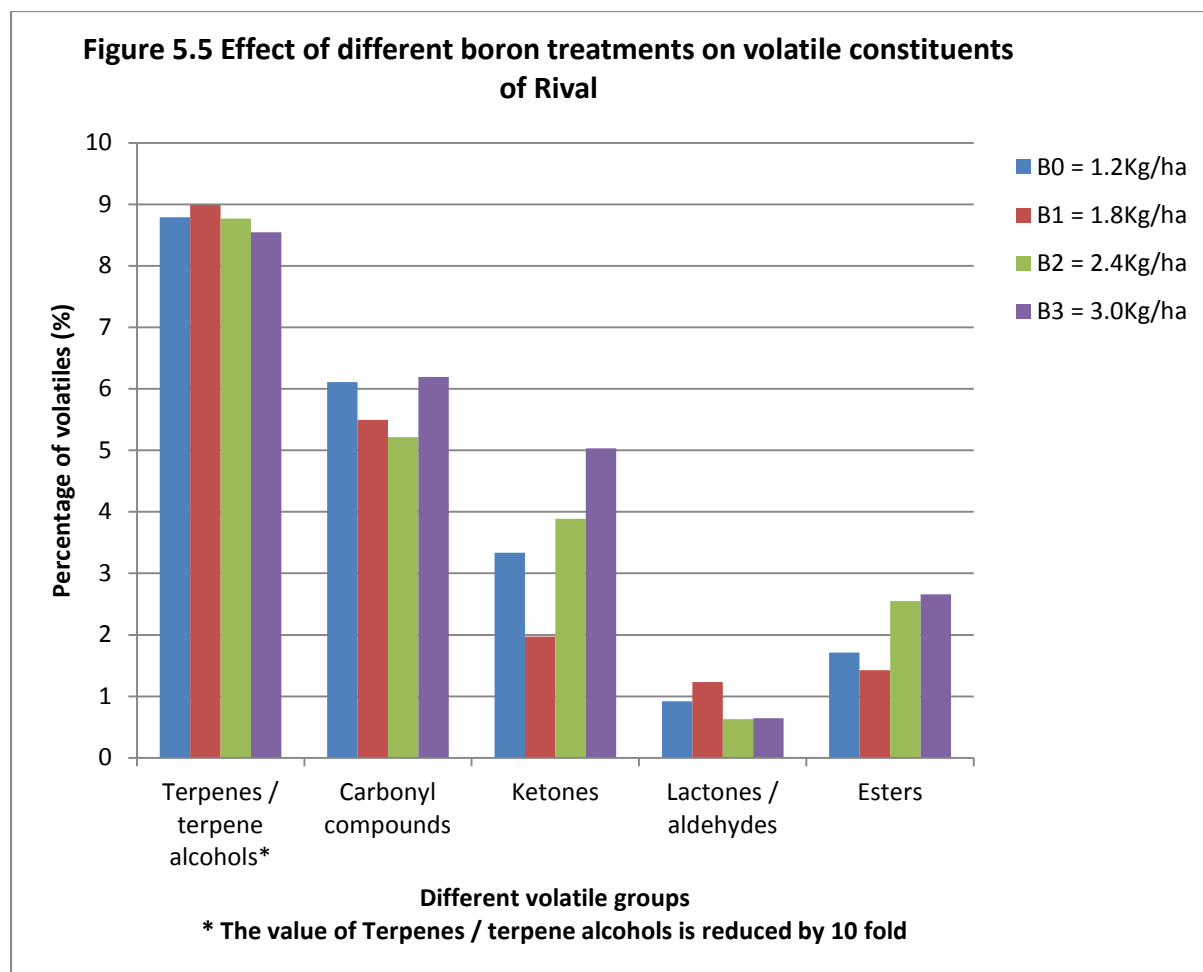
Compounds	No. of VC	Volatiles eluted with HS-SPME	Goldrich	Rival	Orangered® Bhart	Goldrich	Rival	Orangered® Bhart
			Min-Max range (ppm)			Mean value (ppm)		
<b>Esters</b>	1	hexyl acetate	0.02-0.67	0.28-13.42	0.07-0.22	0.28(0.02)	2.68(0.33)	0.15(0.01)
	2	hexyl benzoate	0.02-0.52	0.05-1.39	0.04-0.82	0.13(0.01)	0.38(0.04)	0.17(0.02)
		<b>total</b>				<b>0.41</b>	<b>3.06</b>	<b>0.32</b>
<b>Aldehydes /lactones</b>	3	2 heptenal	0.04-0.45	0.23-4.11	0.08-1.98	0.14(0.01)	0.90(0.08)	0.42(0.05)
	4	$\gamma$ -decalactone	0.02-0.55	0.01-1.13	0.01-0.62	0.08(0.01)	0.21(0.04)	0.05(0.01)
	5	$\gamma$ -dodecalactone	0.01-0.16	0.01-0.07	0.01-0.15	0.05(0.01)	0.02(0.00)	0.03(0.00)
		<b>Total</b>				<b>0.27</b>	<b>1.13</b>	<b>0.50</b>
<b>Ketones</b>	6	$\beta$ -ionone	0.07-2.46	0.22-7.52	0.23-0.23	0.50(0.06)	2.62(0.22)	1.18(0.11)
	7	$\beta$ -ionone epioxide	0.01-0.23	0.01-0.72	0.00-0.47	0.04(0.01)	0.55(0.02)	0.09(0.01)
	8	$\alpha$ -terpenone	0.10-2.50	0.23-15.90	0.26-5.92	0.58(0.09)	1.87(0.33)	1.25(0.16)
	9	geranyl acetone	0.08-0.85	0.04-2.56	0.04-1.90	0.25(0.03)	0.15(0.07)	0.27(0.04)
		<b>Total</b>				<b>1.37</b>	<b>5.19</b>	<b>2.79</b>
<b>Carbonyl compounds</b>	10	benzaldehyde	0.06-0.38	0.15-4.08	0.15-2.30	0.18(0.01)	0.66(0.09)	0.44(0.05)
	11	6 methyl hept 5-en-2-one	0.03-0.56	0.32-4.07	0.11-2.38	0.19(0.02)	1.00(0.15)	0.46(0.06)
	12	C10H16	0.09-0.77	0.18-4.30	0.11-3.90	0.24(0.02)	1.78(0.11)	0.79(0.10)
	13	C10H16	0.06-0.94	0.14-5.75	0.06-6.28	0.27(0.02)	0.50(0.15)	1.10(0.16)
	14	C10H16O	0.15-2.16	0.20-6.44	0.08-4.03	1.01(0.06)	1.18(0.19)	1.11(0.11)
	15	Hexanal	0.07-0.39	0.20-1.93	0.10-2.73	0.20(0.01)	1.72(0.05)	0.56(0.06)
	16	E-2 Octenal	0.02-1.50	0.10-1.63	0.10-0.95	0.22(0.04)	1.76(0.04)	0.35(0.03)
		<b>Total</b>				<b>2.31</b>	<b>8.60</b>	<b>4.81</b>
Concentrations expressed relative to internal standard 0.1 mg fenchone. Results are for inter comparison only. Percent recoveries and FID response factors were not determined for each compound (assume all response factors = 1).								

**Table 5.4** Minimum and maximum range and mean values of volatile compounds of three different apricot cultivars treated with four levels of boron and ReTain®

Compounds	No of VC	Volatiles eluted with HS-SPME	Goldrich	Rival	Orangered® Bhart	Goldrich	Rival	Orangered® Bhart
			Min-Max range (ppm)			Mean value (ppm)		
<b>Terpenes/ Terpene alcohols</b>	17	myrcene	0.32-4.54	1.86-57.24	1.90-48.37	1.88(0.12)	11.14(1.21)	8.73(1.21)
	18	$\alpha$ -phellandrene	0.12-1.38	0.29-11.25	0.25-6.97	0.41(0.04)	2.02(0.22)	1.37(0.16)
	19	p-cymene	0.39-10.59	0.64-48.39	0.26-9.51	2.32(0.48)	4.93(1.02)	2.36(0.28)
	20	limonene	0.31-6.98	2.69-195.55	0.34-91.33	2.94(0.23)	22.02(3.97)	12.38(2.01)
	21	cis- $\beta$ -ocimene	0.28-2.25	0.67-9.38	0.11-24.16	0.70(0.05)	4.05(0.33)	3.36(0.55)
	22	trans - $\beta$ -ocimene	0.12-1.62	0.12-7.47	0.09-9.65	0.55(0.04)	2.47(0.22)	1.91(0.27)
	23	terpinolene	0.19-3.66	0.18-8.92	0.28-6.61	0.69(0.09)	2.29(0.28)	1.77(0.22)
	24	linalool	0.56-12.53	8.34-89.13	3.99-187.02	5.74(0.37)	47.23(2.65)	40.65(4.57)
	25	Ocimenol isomer	0.04-1.14	0.09-5.00	0.02-2.12	0.20(0.03)	0.83(0.11)	0.40(0.06)
	26	Ocimenol isomer	0.01-1.71	0.06-7.94	0.03-1.98	0.24(0.04)	1.12(0.18)	0.35(0.05)
	27	Terpinene 4-ol	0.03-0.95	0.08-1.32	0.05-1.54	0.18(0.02)	0.57(0.04)	0.30(0.04)
	28	$\alpha$ -terpineol	0.02-15.76	4.84-62.95	1.65-98.45	4.59(0.48)	28.26(2.08)	18.51(2.36)
	29	p menthen-9-ol	0.12-1.35	0.08-2.71	0.05-2.69	0.62(0.04)	1.01(0.09)	0.71(0.09)
	30	nerol	0.03-2.65	0.04-4.38	0.08-8.07	0.37(0.06)	0.98(0.16)	1.63(0.21)
	31	geraniol	0.05-2.65	0.57-13.75	0.04-24.32	0.78(0.07)	5.12(0.49)	4.42(0.67)
	32	Geranial	0.01-0.95	0.04-2.20	0.02-2.30	0.15(0.02)	0.63(0.06)	0.40(0.05)
	33	Dihydroactinidiolide	0.01-0.13	0.03-0.70	0.01-0.26	0.05(0.00)	0.17(0.02)	0.08(0.01)
	34	Nerolidol	0.00-0.19	0.02-3.87	0.01-0.57	0.07(0.01)	0.22(0.08)	0.09(0.01)
		<b>Total</b>				<b>22.48</b>	<b>135.06</b>	<b>99.42</b>

Concentrations expressed relative to internal standard 0.1 mg fenchone. Results are for inter comparison only. Percent recoveries and FID response factors were not determined for each compound (assume all response factors = 1).





Terpene and terpene alcohols were produced with the highest relative abundance for all the different boron and variety treatments. These constitute ~75-93 % of total volatiles quantified followed by carbonyl compounds ~4-10%, ketones ~1.7-5.1%, lactones and aldehydes ~ 0.3-1.2%, and esters ~ 0.2-3% across the three varieties. The volatile fraction of apricot shows a considerable variability for the concentration of the aromatic compounds isolated from different varieties, though Goldrich had a greater proportional diversity of non terpene compounds (Table 5.4). These compounds have been previously reported to be important compounds in creating the characteristic apricot aroma. Linalool, cymene,  $\alpha$ -phellandrene, limonene, terpinolene, geraniol, myrcene and  $\alpha$ -terpineol were the predominant terpenes and terpene alcohols produced in all three varieties.

Nevertheless, the distribution of volatiles within the 3 cultivars was greatly different. Terpenes were at a maximum ~90-93 % in Orangered® Bhart and ~85-90% in Rival and ~75-85% in Goldrich. The increasing boron treatments have significantly ( $P = 0.002$ ) affected terpenes of the Goldrich variety as mentioned in Table 5.5. The absolute level of terpenes increased from 19.0 ppm to 29.5 ppm from the lowest to highest boron treatment. The level increased from 75% of volatiles in the control to 85 % in the highest boron treated samples as shown in Figure 5.3.

Table 5.5 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different boron treatments of Goldrich variety								
Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	B0 <sup>b</sup>	B1 <sup>b</sup>	B2 <sup>b</sup>	B3 <sup>b</sup>			
esters	hexyl acetate	0.11	0.15	0.09	0.13	0.02 – 0.24	0.362	0.782
	hexyl benzoate	0.08	0.04	0.08	0.13	0.02 – 0.20		
	Total	<b>0.19</b>	<b>0.19</b>	<b>0.17</b>	<b>0.26</b>			
Lactones / aldehydes	2 heptenal	0.12	0.11	0.08	0.08	0.04 – 0.21	1.711	0.241
	γ-decalactone	0.12	0.09	0.07	0.10	0.03 – 0.20		
	γ-dodecalactone	n.d	n.d	n.d	n.d	n.d		
	Total	<b>0.24</b>	<b>0.20</b>	<b>0.15</b>	<b>0.18</b>			
Ketones	β-ionone	1.41	0.18	0.18	0.17	0.07 – 2.46	44.643	0.000***
	β-ionone epoxide	0.13	n.d	n.d	n.d	0.05 – 0.23		
	α-terpenone	1.38	1.75	1.74	1.14	0.46 – 2.50		
	geranyl acetone	0.46	n.d	n.d	n.d	0.11 – 0.85		
	Total	<b>3.38</b>	<b>1.93</b>	<b>1.92</b>	<b>1.31</b>			
Carbonyl compounds	benzaldehyde	0.12	0.29	0.33	0.30	0.07 – 0.38	1.224	0.362
	6 methyl hept 5-en-2-one	0.20	0.21	0.21	0.22	0.09 – 0.32		
	C10H16	0.36	0.27	0.31	0.41	0.09 – 0.77		
	C10H16	0.40	0.30	0.34	0.45	0.06 – 0.94		
	C10H16O	0.46	1.15	1.19	1.16	0.15 – 1.50		
	hexanal	0.15	0.16	0.14	0.13	0.07 – 0.23		
	E-2 octenal	0.69	0.40	0.53	0.62	0.07 – 1.50		
	Total	<b>2.38</b>	<b>2.78</b>	<b>3.05</b>	<b>3.29</b>			
Terpenes / terpene alcohols	myrcene	0.75	1.26	1.21	1.32	0.32 – 1.69	12.254	0.002**
	α-phellandrene	0.60	0.55	0.42	0.77	0.26 – 0.91		
	p-cymene	1.54	8.10	9.70	8.82	0.58 – 10.59		
	limonene	0.69	5.20	4.76	6.07	0.31 – 6.80		
	cis-β-ocimene	1.25	1.07	0.91	1.10	0.46 – 2.25		
	trans-β-ocimene	0.60	0.46	0.38	0.39	0.12 – 1.26		
	terpinolene	1.63	0.94	1.00	1.14	0.25 – 3.66		
	linalool	7.18	5.21	4.02	8.45	0.56 – 10.66		
	ocimenol isomer	0.08	0.05	0.10	0.15	0.04 – 0.17		
	ocimenol isomer	0.02	0.04	0.05	0.12	0.01 – 0.13		
	terpinene 4-ol	0.17	0.15	0.20	0.23	0.03 – 0.39		
	α-terpineol	0.49	0.03	0.06	0.09	0.02 – 0.83		
	p menthen-9-ol	0.49	0.34	0.41	0.51	0.12 – 0.66		
	nerol	1.42	0.06	0.08	0.11	0.03 – 2.65		
	geraniol	1.42	0.07	0.07	0.10	0.05 – 2.65		
	geranial	0.57	0.01	0.02	0.02	0.01 – 0.95		
	dihydroactinidiolide	0.06	0.04	0.07	0.08	0.02 – 0.13		
	nerolidol	0.08	0.08	0.11	0.07	0.01 – 0.19		
	Total	<b>19.04</b>	<b>23.66</b>	<b>23.57</b>	<b>29.54</b>			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\*Moderately significant, \*\*\* Highly significant at p<0.05. n.d - Not determined.

Table 5.6 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different boron treatments of Orangered® Bhart variety

Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	B0 <sup>b</sup>	B1 <sup>b</sup>	B2 <sup>b</sup>	B3 <sup>b</sup>			
esters	hexyl acetate	n.d	n.d	n.d	n.d	n.d	0.901	0.482
	hexyl benzoate	0.07	0.08	0.36	0.10	0.04 – 0.82		
	Total	<b>0.07</b>	<b>0.08</b>	<b>0.36</b>	<b>0.10</b>			
Lactones / aldehydes	2 heptenal	0.21	0.34	0.82	0.19	0.16 – 1.98	3.342	0.077
	γ-decalactone	0.02	0.09	0.24	0.04	0.01 – 0.62		
	γ-dodecalactone	0.02	0.02	0.08	0.02	0.01 – 0.15		
	Total	<b>0.25</b>	<b>0.45</b>	<b>1.14</b>	<b>0.25</b>			
Ketones	β-ionone	0.41	0.53	2.05	0.65	0.23 – 3.67	0.899	0.483
	β-ionone epoxide	0.03	0.07	0.22	0.02	0.01 – 0.47		
	α-terpenone	0.56	2.49	2.45	1.03	0.33 – 5.92		
	geranyl acetone	0.09	0.20	0.84	0.07	0.05 – 1.90		
	Total	<b>1.09</b>	<b>3.29</b>	<b>5.56</b>	<b>1.77</b>			
Carbonyl compounds	benzaldehyde	0.27	0.24	0.97	0.35	0.17 – 2.30	2.097	0.179
	6 methyl hept 5-en-2-one	0.24	0.25	0.98	0.40	0.16 – 2.38		
	C10H16	0.47	0.51	1.80	0.46	0.25 – 3.90		
	C10H16	0.65	0.76	2.82	1.51	0.37 – 6.28		
	C10H16O	0.48	0.50	2.04	0.62	0.24 – 4.03		
	hexanal	0.49	0.40	1.15	0.55	0.23 – 2.73		
	E-2 octenal	0.56	0.18	0.41	0.23	0.10 – 0.80		
	Total	<b>3.16</b>	<b>2.84</b>	<b>10.17</b>	<b>3.76</b>			
Terpenes / terpene alcohols	myrcene	5.38	5.08	16.25	6.56	2.82 – 35.66	0.707	0.574
	α-phellandrene	0.93	0.93	3.04	1.34	0.54 – 6.97		
	p-cymene	1.55	1.75	2.08	2.93	0.58 – 6.40		
	limonene	8.16	9.73	35.77	17.05	2.63 – 91.33		
	cis-β-ocimene	4.89	2.69	9.72	1.61	0.78 – 24.16		
	trans-β-ocimene	1.11	1.47	4.80	0.58	0.12 – 9.65		
	terpinolene	0.45	1.10	3.23	1.44	0.28 – 5.61		
	linalool	26.37	25.66	87.11	26.95	13.08 – 187.02		
	ocimenol isomer	0.13	0.24	0.88	0.26	0.06 – 1.97		
	ocimenol isomer	0.12	0.27	1.00	0.30	0.07 – 1.98		
	terpinene 4-ol	0.16	0.21	0.71	0.23	0.09 – 1.54		
	α-terpineol	9.71	15.54	46.48	14.75	5.10 – 98.45		
	p menthen-9-ol	0.27	0.38	1.52	0.52	0.13 – 2.69		
	nerol	0.91	1.35	4.00	0.52	0.08 – 8.07		
	geraniol	0.79	3.97	11.75	1.18	0.04 – 24.32		
	geranial	0.09	0.36	1.08	0.20	0.02 – 2.30		
	dihydroactinidiolide	n.d	0.04	0.13	0.02	0.01 – 0.26		
	nerolidol	0.03	0.05	0.26	0.09	0.02 – 0.57		
	Total	<b>61.05</b>	<b>70.82</b>	<b>229.81</b>	<b>76.53</b>			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\* Moderately significant, \*\*\* Highly significant at p<0.05. n.d -Not determined

Table 5.7 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different boron treatments of Rival variety

Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	B0 <sup>b</sup>	B1 <sup>b</sup>	B2 <sup>b</sup>	B3 <sup>b</sup>			
esters	Hexyl acetate	1.89	0.75	7.01	4.10	0.43 – 13.42	0.946	0.463
	Hexyl benzoate	0.30	0.12	0.68	0.70	0.05 – 1.39		
	Total	<b>2.19</b>	<b>0.87</b>	<b>7.70</b>	<b>4.80</b>			
Lactones / aldehydes	2 Heptenal	0.70	0.46	1.81	0.70	0.23 – 4.11	0.875	0.493
	γ-decalactone	0.41	0.16	0.36	0.24	0.02 – 0.96		
	γ-dodecalactone	0.02	0.01	0.03	0.01	0.01 – 0.06		
	Total	<b>1.13</b>	<b>0.63</b>	<b>2.21</b>	<b>0.95</b>			
Ketones	β-ionone	2.03	0.50	4.22	1.79	0.22 – 7.52	12.073	0.002**
	β-ionone epoxide	0.02	0.06	0.22	0.39	0.01 – 0.72		
	α-terpenone	2.12	0.64	7.09	4.67	0.29 – 15.90		
	Geranyl acetone	0.35	0.10	0.83	0.57	0.04 – 1.21		
	Total	<b>4.52</b>	<b>1.30</b>	<b>12.36</b>	<b>7.42</b>			
Carbonyl compounds	Benzaldehyde	1.06	0.43	1.96	0.81	0.28 – 4.08	0.986	0.447
	6 methyl hept 5-en-2-one	2.26	0.74	2.68	2.38	0.32 – 3.41		
	C10H16	1.00	0.37	1.91	1.40	0.21 – 3.20		
	C10H16	1.56	0.44	3.11	2.10	0.14 – 5.75		
	C10H16O	1.40	0.55	3.02	1.33	0.20 – 5.84		
	Hexanal	0.47	0.63	1.18	0.50	0.26 – 1.93		
	E-2 octenal	0.26	0.27	0.84	0.57	0.11 – 1.63		
	Total	<b>8.01</b>	<b>3.43</b>	<b>14.71</b>	<b>9.09</b>			
Terpenes / terpene alcohols	Myrcene	9.28	4.34	26.99	11.26	1.86 – 57.24	5.297	0.026*
	α-phellandrene	2.01	1.02	4.90	2.39	0.64 – 11.25		
	p-cymene	4.12	1.69	19.12	3.53	0.86 – 48.39		
	Limonene	23.82	9.07	73.87	26.49	3.29 – 195.55		
	Cis-β-ocimene	4.22	1.51	4.80	4.08	1.26 – 5.84		
	Trans-β-ocimene	2.13	0.45	2.74	2.54	0.12 – 4.18		
	Terpinolene	2.36	0.44	2.99	2.73	0.18 – 4.70		
	Linalool	33.46	24.94	57.11	44.40	9.65 – 67.04		
	Ocimenol isomer	1.26	0.21	0.80	0.63	0.09 – 2.47		
	Ocimenol isomer	1.65	0.21	1.40	0.85	0.06 – 3.49		
	Terpinene 4-ol	0.71	0.24	0.72	0.57	0.08 – 1.30		
	α-terpineol	27.60	12.04	41.72	21.28	4.84 – 58.54		
	p menthen-9-ol	0.78	0.21	1.31	0.82	0.08 – 1.84		
	Nerol	1.12	0.78	2.15	1.86	0.34 – 4.21		
	Geraniol	3.05	2.03	5.61	5.08	0.89 – 11.43		
	Geranial	0.41	0.33	1.24	0.54	0.14 – 2.20		
	Dihydroactinidiolide	0.16	0.09	0.33	0.12	0.05 – 0.70		
	Nerolidol	0.18	0.22	0.25	1.37	0.03 – 3.87		
	Total	<b>118.32</b>	<b>59.82</b>	<b>248.05</b>	<b>24.46</b>			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\* Moderately significant, \*\*\* Highly significant at p<0.05. n.d - Not determined.

While the total amount of terpenes increased with the increase in boron in Goldrich variety the results were different in Rival where the percentage decreased with boron treatment and absolute values were highest in the mid-range treatments ( $P=0.026$ ). Orangered® Bhart gave no significant changes to either percentage or level of terpenes.

### **5.4.2 Esters**

Boron increased the esters from 1.7% to 2.6% in the Rival variety. This was a result of the reduction of percentage of terpenes as there was no significant increase in total level (Table 5.7). As mentioned in Figure 5.4, the minimum amount of esters present was in the Orangered® Bhart variety. Lactones showed no significant difference in levels in any of the treatments (Table 5.5, Table 5.6, Table 5.7). **Esters and lactones** were also predominant in the Rival variety (Table 5.7). Though achieving a significance at best of only  $P=0.077$  (Table 5.6) the highest concentration of boron ( $B_3$ ) increased the total esters and total percentage of esters in all three varieties from ~0.1-2.6 %.

The volatile esters are among the most important groups of compounds that contribute to desirable fruity aromas.  $\beta$ -oxidation of fatty acids and oxidation of fatty acids by lipo oxygenase form straight chain alcohols and acyl-coenzyme A (coA) are the precursors essential for the formation of esters.

Though the increase in esters compared to total volatile content is only a small amount, esters play an important role in apricot flavor so the change could be expected to enhance flavor with boron treatment and is worth further investigation.

It was hoped that the headspace sampling of intact fruit would help to identify compounds responsible for the pleasant fruity apricot aroma (i.e. esters). The variety of esters was notably less in the samples from blended apricots. Levels of esters and more particularly those of butyl and hexyl acetates particularly increase with ripening. Hexyl acetates have been previously described in apricot fruit as banana like, nail polish and solvent like aroma.

### **5.4.3 Ketones**

The ketones significantly decreased in Goldrich ( $P=0.000$ ) variety at higher concentrations of boron treatments. However, ketones in Rival significantly benefited from higher boron concentration treatments and increased significantly from 3.3 % to 5%. 15.9 ppm of  $\alpha$ -terpenone was the highest amount of a ketone recovered and came from the  $B_2$  treatment of Rival. It was difficult to isolate  $\beta$ -ionone epoxide and geranyl acetone in boron treated samples of Goldrich.

$\beta$ -ionone epoxide is also known as  $\beta$ -ionone-5,6-epoxide it has an intensely sweet, fruity-woody odour of great volume and tenacity suggestive of precious woods with floral background notes and similar to raspberry. It is more stable than other ionones and therefore used in soaps and detergents. Geranyl acetones have fresh-floral light but penetrating sweet rosy, Magnolia like odour of moderate

tenacity. This ketone was developed as an intermediate in the synthesis of nerolidol and used in perfume composition particularly in perfume soaps where its superior stability makes it a reliable sweetener in floral composition.

#### **5.4.4 Carbonyl compounds**

Carbonyl compounds tend to increase with inputs of boron in Goldrich and Rival. However, there were no significant differences across the treatments (Tables 5.5-7). There is no significant effect of boron treatment in the Orangered® Bhart variety. Maximum amount of carbonyl compounds were found in Goldrich ~8.4-10.5% and minimum amount of carbonyl compounds were found in Orangered® Bhart ~4-5%. The presence of C<sub>6</sub> compounds was probably due to lipoxygenase activity, action initialized by the disruption of the fruit tissues when blended (Frankel, 1982).

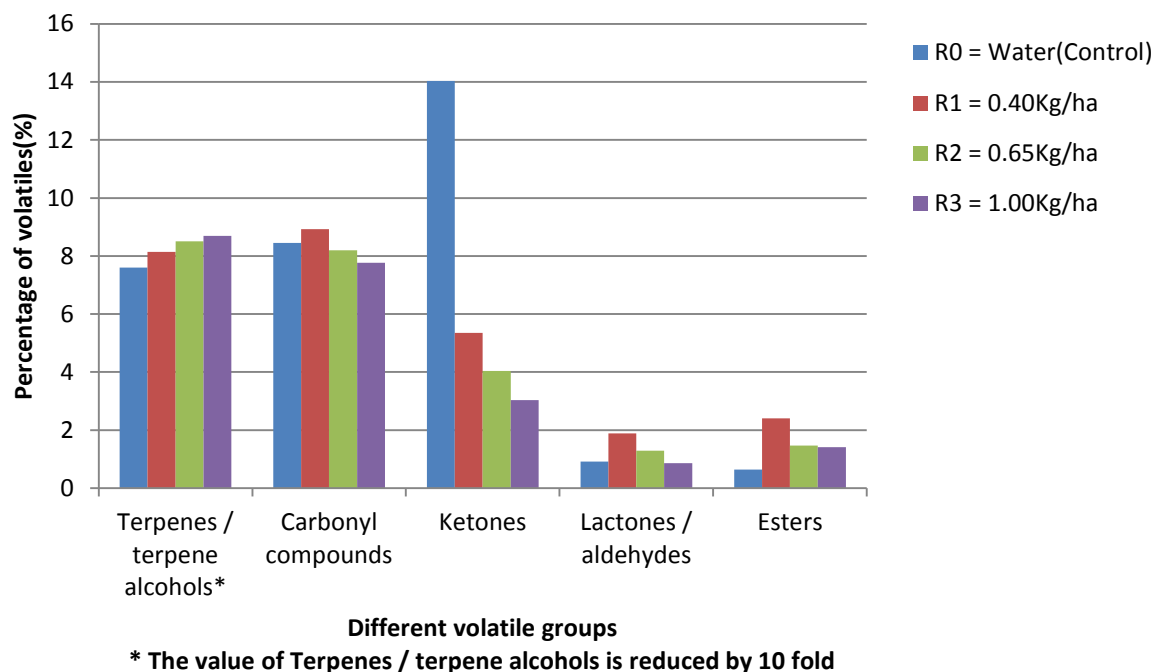
6-methyl-5-hepten-2-one is described to have a floral aroma (Guichard *et al.*, 1990). It has been identified in other fruits such as sweet cherries. It is present in apricots, plums and plumcots and is regarded as a non terpenoid arising from isoprenoid degradation (Takeoka *et al.*, 1988). The compound 6 methyl hept-5-en-2-one is eluted at a maximum at 3.41 ppm in the Rival variety. Though it is found in other varieties, the total amount produced is in small quantities. Treatments that increased this compound may lead to improved aroma characteristics

### **5.5 Individual effects of ReTain® on volatile constituents of three varieties of apricots**

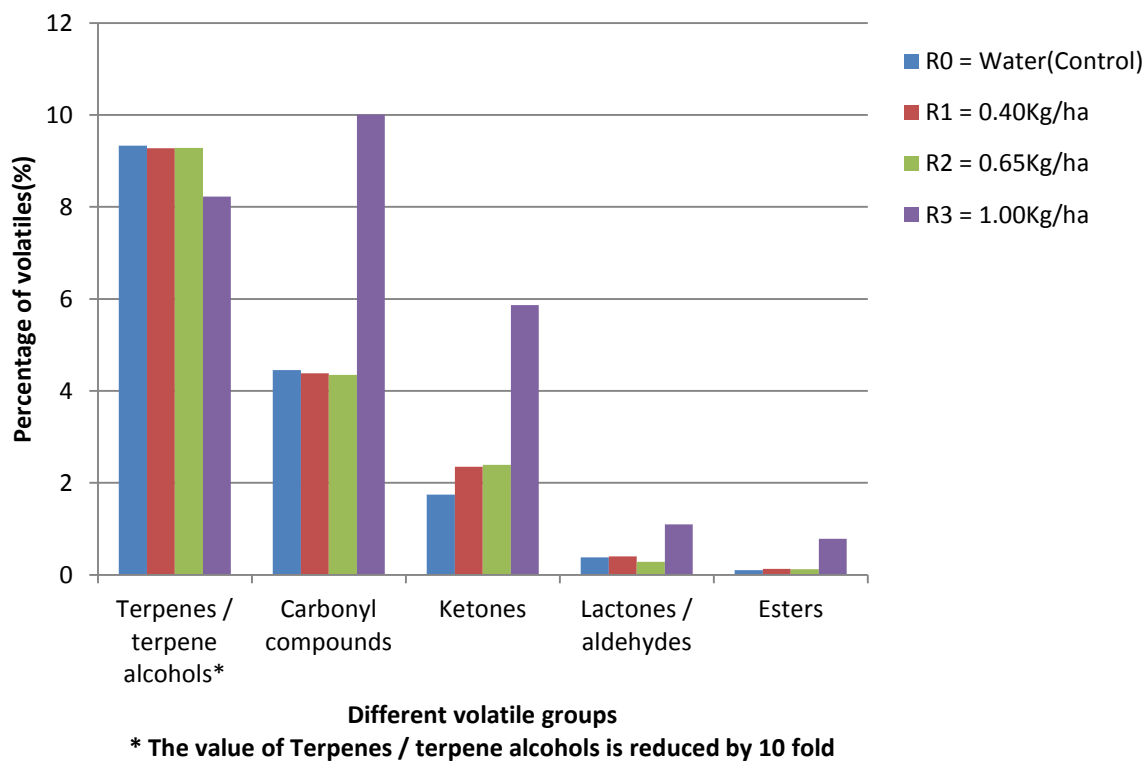
Figures 5.6-8 summarise the data for the effects of ReTain® on the percentages of volatile constituents of apricots. These data are taken from the lowest boron treatments. The full data for the levels of individual and group mean levels along with the statistics for the mean values are presented in Tables 5.8, 5.9 and 5.10. The following discussion considers the effects of variety and ReTain® on the individual groups of compounds.

ReTain® had significant (though not necessarily consistent across varieties) effects on levels of all compounds for Goldrich (except carbonyl) and Orangered® Bhart. The directions for the percentage changes were often opposite for these two varieties (terpenes, carbonyl, ketones). However, there were no significant effects for Rival (Tables 5.8, 5.9 and 5.10).

**Figure 5.6 Effect of different ReTain® treatments on volatile constituents of Goldrich**



**Figure 5.7 Effect of different ReTain® treatments on volatile constituents of Orangered® Bhart**



**Table 5.8 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different ReTain® treatments of Goldrich variety**

Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	R0 <sup>b</sup>	R1 <sup>b</sup>	R2 <sup>b</sup>	R3 <sup>b</sup>			
esters	hexyl acetate	0.11	0.57	0.20	0.19	0.02 – 0.67	31.548	0.000***
	hexyl benzoate	0.08	0.19	0.15	0.09	0.02 – 0.26		
	Total	<b>0.19</b>	<b>0.76</b>	<b>0.35</b>	<b>0.28</b>			
Lactones / aldehydes	2 heptenal	0.12	0.26	0.16	0.10	0.04 – 0.42	6.929	0.013*
	γ-decalactone	0.12	0.34	0.03	0.02	0.02 – 0.55		
	γ-dodecalactone	n.d	0.02	0.12	0.05	0.02 – 0.16		
	Total	<b>0.24</b>	<b>0.62</b>	<b>0.31</b>	<b>0.17</b>			
Ketones	β-ionone	1.41	0.79	0.45	0.33	0.26 – 2.46	51.374	0.000***
	β-ionone epioxide	0.13	0.04	0.03	0.03	0.02 – 0.23		
	α-terpenone	1.38	0.43	0.28	0.17	0.13 – 2.34		
	geranyl acetone	0.46	0.45	0.22	0.10	0.08 – 0.85		
	Total	<b>3.38</b>	<b>1.71</b>	<b>0.98</b>	<b>0.63</b>			
Carbonyl compounds	benzaldehyde	0.12	0.32	0.14	0.06	0.06 – 0.33	0.421	0.743
	6 methyl hept 5-en-2-one	0.20	0.14	0.08	0.32	0.07 – 0.39		
	C10H16	0.36	0.31	0.18	0.12	0.09 – 0.77		
	C10H16	0.40	0.38	0.23	0.16	0.06 – 0.94		
	C10H16O	0.46	1.21	1.12	0.73	0.15 – 1.52		
	hexanal	0.15	0.30	0.16	0.14	0.07 – 0.39		
	E-2 octenal	0.69	0.14	0.08	0.06	0.03 – 1.50		
	Total	<b>2.38</b>	<b>2.80</b>	<b>1.99</b>	<b>1.59</b>			
Terpenes / terpene alcohols	myrcene	0.75	3.21	2.11	1.33	0.32 – 3.39	21.755	0.000***
	α-phellandrene	0.60	0.31	0.41	0.24	0.21 – 0.84		
	p-cymene	1.54	1.09	0.64	0.49	0.45 – 2.96		
	limonene	0.69	3.63	2.25	2.05	0.31 – 4.02		
	cis-β-ocimene	1.25	0.80	0.56	0.48	0.44 – 2.25		
	trans-β-ocimene	0.60	0.90	0.59	0.31	0.12 – 1.26		
	terpinolene	1.63	0.93	0.57	0.28	0.26 – 3.66		
	linalool	7.18	4.51	4.08	0.85	1.65 – 10.66		
	ocimenol isomer	0.08	0.28	0.18	0.11	0.04 – 0.44		
	ocimenol isomer	0.02	0.41	0.29	0.13	0.01 – 0.76		
	terpinene 4-ol	0.17	0.18	0.14	0.10	0.03 – 0.39		
	α-terpineol	0.49	6.77	5.93	4.56	0.23 – 8.68		
	p menthen-9-ol	0.49	0.87	0.93	0.42	0.33 – 1.35		
	nerol	1.42	0.39	0.39	0.33	0.27 – 2.65		
	geraniol	1.42	0.98	1.07	0.95	0.43 – 2.65		
	geranial	0.57	0.15	0.16	0.15	0.11 – 0.95		
	dihydroactinidiolide	0.06	0.07	0.04	0.04	0.02 – 0.13		
	nerolidol	0.08	0.08	0.06	0.03	0.01 – 0.19		
	Total	<b>19.04</b>	<b>25.56</b>	<b>20.40</b>	<b>17.85</b>			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\* Moderately significant, \*\*\* Highly significant at p<0.05. n.d -Not determined



**Table 5.9 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different ReTain® treatments of Orangered® Bhart variety**

Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	R0	R1	R2	R3			
esters	hexyl acetate	n.d	n.d	n.d	n.d	n.d	16.757	0.001**
	hexyl benzoate	0.07	0.11	0.09	0.27	0.04 – 0.27		
	Total	<b>0.07</b>	<b>0.11</b>	<b>0.09</b>	<b>0.27</b>			
Lactones / aldehydes	2 heptenal	0.21	0.24	0.16	0.38	0.10 – 0.61	25.728	0.000***
	γ-decalactone	0.02	0.02	0.01	0.01	0.01 – 0.02		
	γ-dodecalactone	0.02	0.03	0.02	0.02	0.01 – 0.04		
	Total	<b>0.25</b>	<b>0.29</b>	<b>0.19</b>	<b>0.41</b>			
Ketones	β-ionone	0.41	0.87	0.83	1.13	0.30 – 1.54	4.854	0.033*
	β-ionone epioxide	0.03	0.06	0.07	0.05	0.01 – 0.09		
	α-terpenone	0.56	0.71	0.58	0.66	0.31 – 1.21		
	geranyl acetone	0.09	0.15	0.17	0.10	0.04 – 0.20		
	Total	<b>1.09</b>	<b>1.79</b>	<b>1.65</b>	<b>1.94</b>			
Carbonyl compounds	benzaldehyde	0.27	0.24	0.22	0.56	0.15 – 0.73	32.430	0.000***
	6 methyl hept 5-en-2-one	0.24	0.27	0.22	0.75	0.11 – 0.79		
	C10H16	0.47	0.58	0.49	0.34	0.21 – 0.95		
	C10H16	0.65	0.85	0.66	0.35	0.06 – 1.39		
	C10H16O	0.48	0.81	0.83	1.04	0.41 – 1.30		
	hexanal	0.49	0.32	0.38	0.33	0.12 – 0.60		
	E-2 octenal	0.56	0.16	0.16	0.24	0.11 – 0.66		
	Total	<b>3.16</b>	<b>3.23</b>	<b>2.96</b>	<b>3.61</b>			
Terpenes / terpene alcohols	myrcene	5.38	5.31	4.72	2.94	1.95 – 8.04	20.980	0.000***
	α-phellandrene	0.93	0.95	0.77	1.79	0.48 – 1.95		
	p-cymene	1.55	1.90	1.53	1.10	0.65 – 3.28		
	Limonene	8.16	8.74	6.64	4.99	2.63 – 14.49		
	cis-β-ocimene	4.89	3.02	2.17	2.56	0.92 – 8.75		
	trans-β-ocimene	1.11	1.36	0.48	0.72	0.14 – 2.59		
	terpinolene	0.45	1.35	0.97	0.46	0.28 – 2.26		
	linalool	26.37	29.68	32.16	10.70	3.99 – 51.20		
	ocimenol isomer	0.13	0.25	0.18	0.13	0.02 – 0.46		
	ocimenol isomer	0.12	0.29	0.12	0.12	0.03 – 0.44		
	terpinene 4-ol	0.16	0.21	0.18	0.27	0.07 – 0.55		
	α-terpineol	9.71	12.94	10.43	2.97	1.65 – 20.67		
	p menthen-9-ol	0.27	0.57	0.38	0.11	0.10 – 0.90		
	nerol	0.91	1.23	0.90	0.27	0.17 – 1.89		
	geraniol	0.79	3.55	2.37	1.09	0.33 – 5.58		
	geranial	0.09	0.30	0.20	0.25	0.06 – 0.42		
	dihydroactinidiolide	0.00	0.06	0.07	0.05	0.01 – 0.09		
	nerolidol	0.03	0.06	0.04	0.10	0.02 – 0.14		
	Total	<b>61.05</b>	<b>71.77</b>	<b>64.31</b>	<b>30.62</b>			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\* Moderately significant, \*\*\* Highly significant at p<0.05. n.d- Not determined

Table 5.10 Concentrations of volatile (in ppm equivalent of fenchone) compounds for four different ReTain® treatments of Rival variety

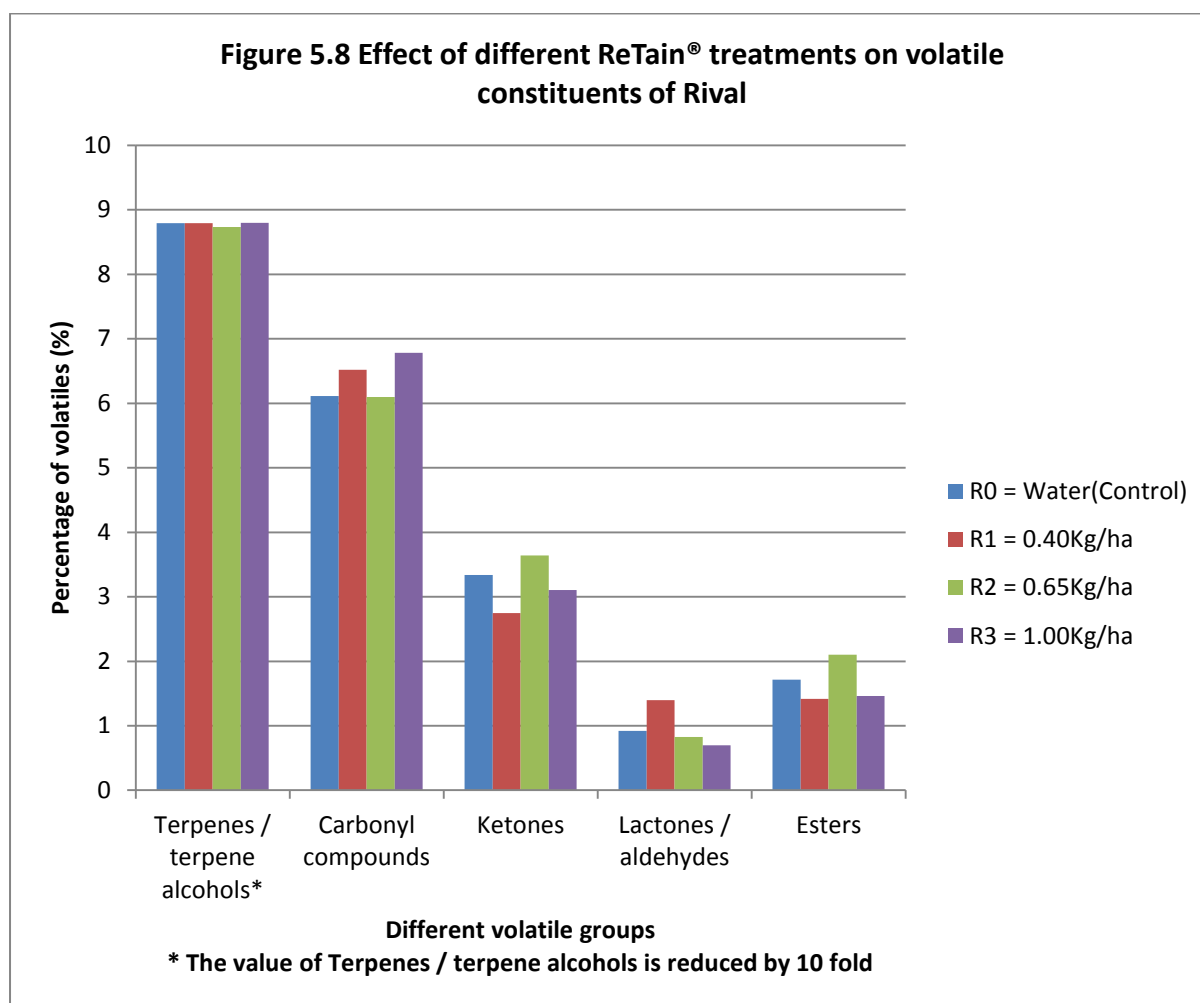
Volatiles		Mean				Range	F-value	Significance
Group of compounds	Compounds	R0 <sup>b</sup>	R1 <sup>b</sup>	R2 <sup>b</sup>	R3 <sup>b</sup>			
esters	hexyl acetate	1.89	0.82	3.35	1.40	0.63 – 3.86	2.454	0.138
	hexyl benzoate	0.30	0.14	0.40	0.19	0.11 – 0.46		
	Total	2.19	0.96	3.75	1.59			
Lactones / aldehydes	2 heptenal	0.70	0.53	1.33	0.57	0.33 – 1.39	1.420	0.307
	γ-decalactone	0.41	0.29	0.12	0.09	0.01 – 0.83		
	γ-dodecalactone	0.02	0.01	0.01	0.01	0.01 – 0.03		
	Total	1.13	0.83	1.46	0.67			
Ketones	β-ionone	2.03	0.82	2.07	0.95	0.53 – 3.54	1.812	0.223
	β-ionone epoxide	0.02	0.01	0.02	0.08	0.01 – 0.10		
	α-terpenone	2.12	1.06	3.46	1.96	0.55 – 3.97		
	geranyl acetone	0.35	0.14	0.91	0.16	0.04 – 1.77		
	Total	4.52	2.03	6.46	3.15			
Carbonyl compounds	benzaldehyde	1.06	0.79	1.51	0.59	0.45 – 1.56	0.109	0.953
	6 methyl hept 5-en-2-one	2.26	1.01	2.48	1.44	0.75 – 3.23		
	C10H16	1.00	0.51	1.27	1.81	0.32 – 4.30		
	C10H16	1.56	0.78	1.82	0.97	0.53 – 1.95		
	C10H16O	1.40	0.70	2.55	0.93	0.40 – 2.57		
	hexanal	0.47	0.37	0.70	0.46	0.24 – 0.82		
	E-2 octenal	0.26	0.47	0.50	0.34	0.19 – 0.70		
	Total	8.01	4.63	10.83	6.54			
Terpenes / terpene alcohols	myrcene	9.28	5.03	11.51	6.38	2.87 – 12.22	0.057	0.981
	α-phellandrene	2.01	1.06	1.92	1.42	0.65 – 2.30		
	p-cymene	4.12	2.92	4.20	1.53	0.83 – 6.63		
	limonene	23.82	12.98	11.72	17.03	2.93 – 38.71		
	cis-β-ocimene	4.22	1.79	4.07	4.74	0.67 – 6.43		
	trans-β-ocimene	2.13	0.75	3.10	1.66	0.22 – 3.67		
	terpinolene	2.36	0.92	4.53	1.31	0.32 – 4.74		
	linalool	33.46	23.23	68.82	34.22	8.34 – 75.97		
	ocimenol isomer	1.26	0.42	0.97	0.48	0.17 – 2.47		
	ocimenol isomer	1.65	0.46	1.35	0.53	0.15 – 3.49		
	terpinene 4-ol	0.71	0.33	0.70	0.43	0.18 – 1.14		
	α-terpineol	27.60	14.00	33.23	18.30	7.41 – 46.40		
	p menthen-9-ol	0.78	0.97	1.12	0.74	0.41 – 1.19		
	nerol	1.12	0.10	0.25	0.09	0.05 – 2.32		
	geraniol	3.05	1.43	6.77	2.98	0.57 – 6.84		
	geranial	0.41	0.35	0.73	0.17	0.04 – 0.86		
	dihydroactinidiolide	0.16	0.03	0.13	0.06	0.03 – 0.24		
	nerolidol	0.18	0.13	0.11	0.05	0.02 – 0.28		
	Total	118.32	66.90	155.23	92.12			

<sup>b</sup> Percentage composition given in table 5.3. \* Low significant, \*\*Moderately significant, \*\*\* Highly significant at p<0.05. n.d- Not determined

### 5.5.1 Terpene and terpene alcohols

The total terpenes isolated were 75%-93% of the volatiles which is similar to the values obtained for the boron treatments. Terpene and terpene alcohols were produced with the highest relative abundance for all the different ReTain® and variety treatments. These constitutes ~75-93 % of total volatiles quantified followed by carbonyl compounds ~4-10%, ketones ~1.7-14%, lactones and aldehydes ~ 0.3-1.8%, and esters ~ 0.1-2.4% in all three varieties.

Terpenes contents are highly significantly affected ( $P < 0.000$ ) by the addition of ReTain® for Goldrich and Orangered® Bhart variety. The maximum amount of individual terpene compounds was produced from the Rival variety. In all three varieties, linalool is the maximum recovered terpene followed by  $\alpha$ -terpineone and limonene. The levels of myrcene and cis- $\beta$ -ocimene were similar in the Rival variety. There was no effect of  $R_0$ ,  $R_1$  and  $R_2$  on the terpene or terpene alcohols of Orangered® Bhart and Rival varieties. There was a 14.5 % increase in total amount of terpenes and terpene alcohols in Goldrich at the maximum level of Retain® which might have considerably decreased the amount of ketones in the tested samples.



### 5.5.2 Other groups

As shown in Fig 5.6 the addition of ReTain® has significantly decreased ketones by up to 75% while increasing the level of terpenes from 7.59 to 8.69 % in Goldrich. Conversely the R<sub>3</sub> treatment has increased ketones by five times in Orangered® Bhart compared with the control while having no effect at other concentrations or in Rival. The R<sub>3</sub> concentration had a significant effect on carbonyl compounds, ketones, lactones and esters in the Orangered® Bhart variety, which may indicate an external factor confounded this treatment. This variety behaved differently to the other varieties for the effect of ReTain®.

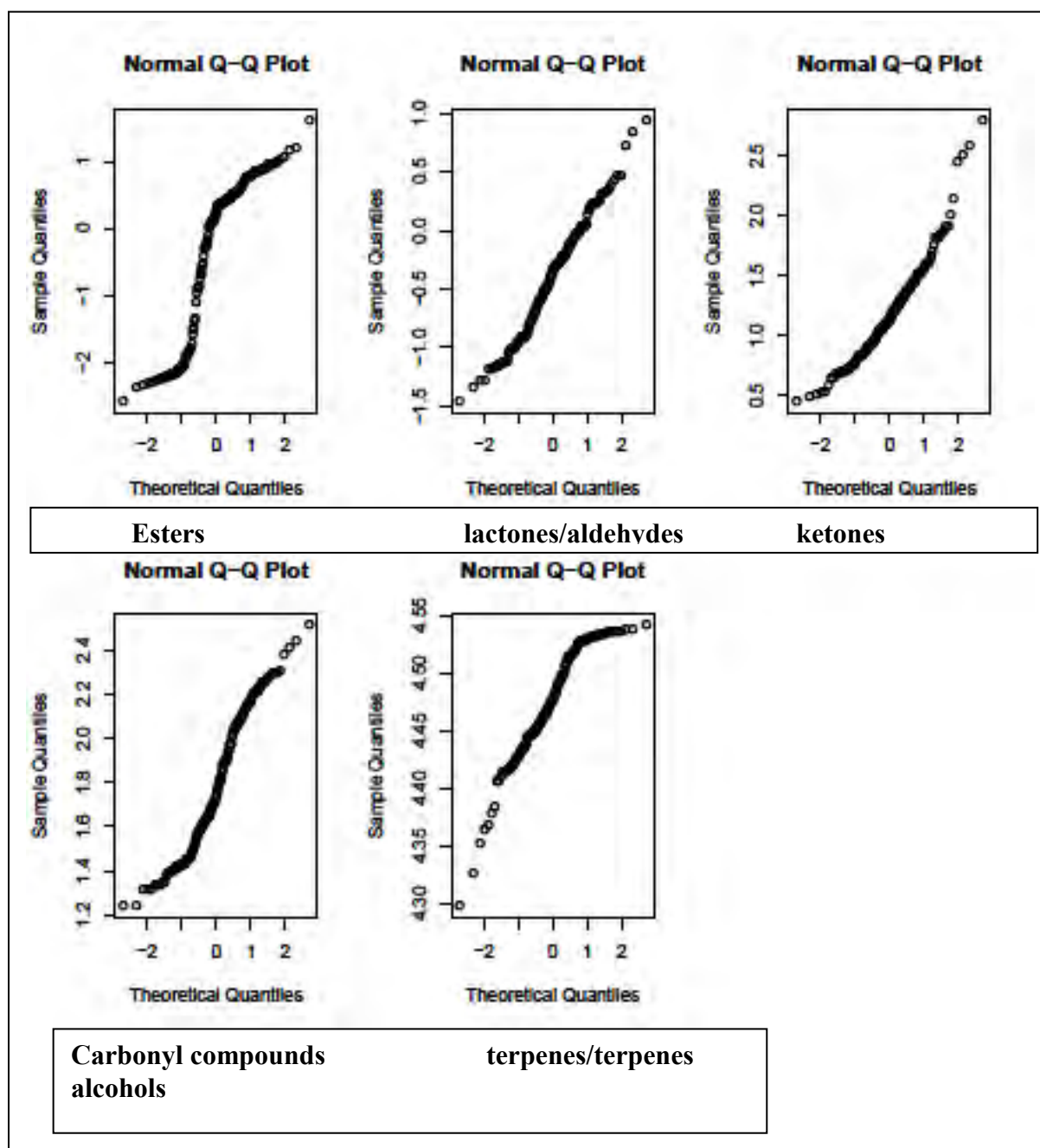
As indicated the R<sub>3</sub> treatment of the Orangered® Bhart variety with ReTain® significantly increased the carbonyl compound by ~60% and decreased the terpenes. Other treatments with ReTain® did not have significant effects on levels of the carbonyl group in Orangered® Bhart. However, in Goldrich and Rival varieties the carbonyl compounds were not significantly affected by the treatments of ReTain®.

Lactones were highly significant increased by ReTain® treatment in Orangered® Bhart ( $P = 0.000$ ) and Goldrich ( $P=0.013$ ). The increase is three times with ReTain® treatment for R<sub>3</sub> Orangered® Bhart. In Goldrich, the R<sub>1</sub> treatments increased the level of lactones especially decalactone and 2-hexanal compared to other treatments. Thus the optimal level of ReTain® was not consistent.

For Rival, ReTain® had minor treatment effects on ketones and carbonyl compounds, none of which were significant. Though the amount of volatiles produced in Rival was the most of the 3 varieties there was no major treatment effect of ReTain®.

To visually assess the fit of aroma distributions to a theoretical normal distribution, quantile-quantile (Q-Q) plots were constructed in SPSS software. The Q-Q plots presented the quantiles of individual volatile group and Retain® treatment effect against the quantiles of a theoretical normal distribution. The volatile group and ReTain® treatment effect are deemed to approximate a theoretical normal distribution when the plot clusters around a straight line.

Figure 5.9 The Normality plot of volatiles of Rival



Representative normality plots of volatiles of Rival variety in the order of esters, lactones and aldehydes, ketones, carbonyl compounds and terpenes/terpene alcohols. Data for other varieties were similar indicating statistical analysis techniques used were appropriate.

## 5.6 Combined effects of boron and ReTain® on volatile constituents of apricots

The individual effects of the boron and ReTain® treatments were different from the combined effects of the interaction of boron and ReTain® (significant interactions in 11/15 instances more than for boron or retain alone). As shown in the Figure 5.10a, Figure 5.11a and Figure 5.12a which presents the individual effects of boron and ReTain® and the interaction effects on percentages of volatile groups of carbonyl compounds, lactones, ketones and esters. As terpenes are produced in large amounts, it was not possible to present them on the same scale. Figures 5.10b-11b-12b represents the total percentage of terpenes and terpene alcohols eluted in the same samples. All of the results were statistically analysed and are represented in Table 5.11. Each volatile group is represented for the percentage of specific group of a specific variety for each treatment.

The individual effects of boron were predominant in Goldrich where especially ketones and terpene groups behaved differently. However, for ReTain® both Goldrich and Orangered® Bhart variety were significantly affected. Most of the volatile groups for both varieties were either moderate to high significantly affected by the treatments. This behaviour of volatile groups proves that the effect of Retain® was more prominent (9/15 highly significant) than the effect of boron (2/15 highly significant).

Figure 5.10a Effect of different treatments on volatile constituents of Goldrich

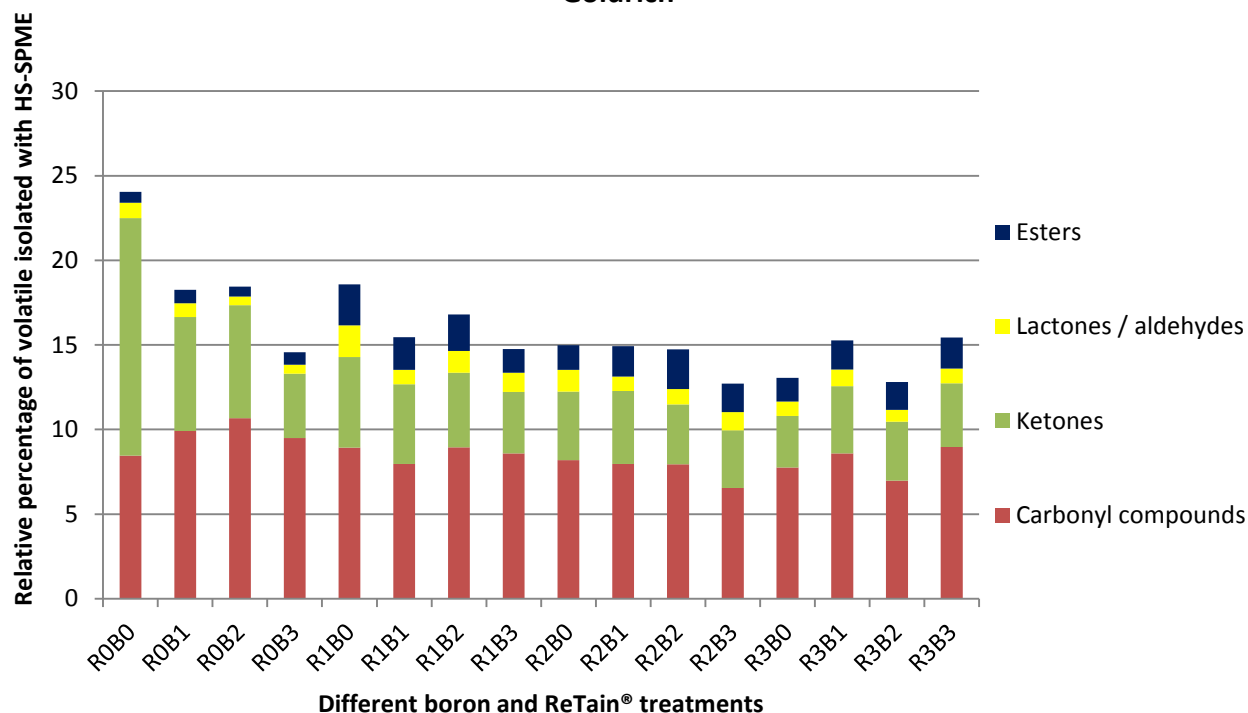


Figure 5.10a Relative proportions (percent) of the main classes of volatile compounds in the different boron and ReTain® treatments of Goldrich apricot variety. Concentrations of Treatments **Boron**: B0=1.2 Kg / ha, B1= 1.8 Kg/ ha, B2= 2.4 Kg/ ha, B3= 3.0 kg/ ha, **ReTain®**: R0= Water (control), R1 = 0.40 Kg/ ha, R2= 0.65 Kg/ ha, R3= 1.00 Kg/ ha.

Figure 5.10b Effect of different treatments on Terpenes / terpene alcohols of Goldrich

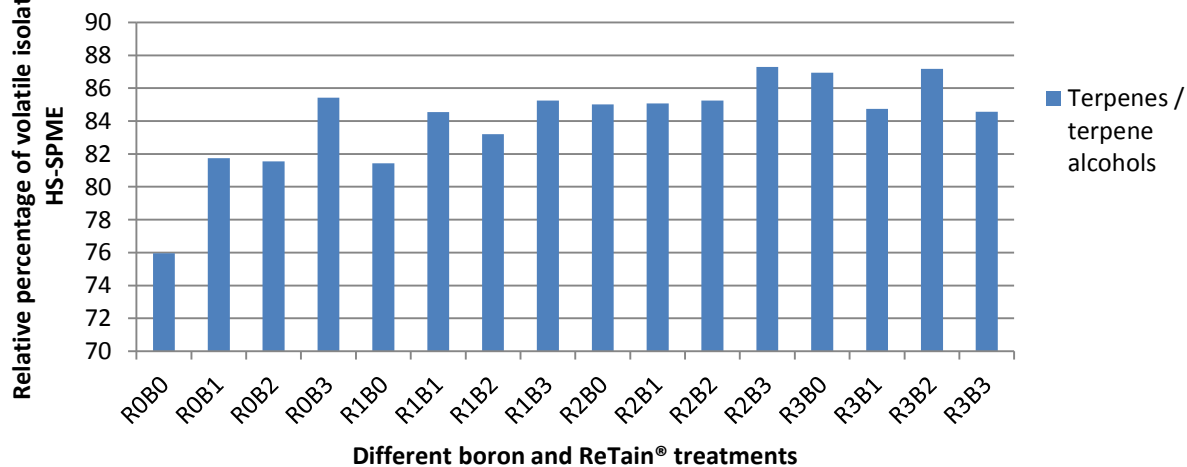


Figure 5.10b Relative proportions (percent) of terpenes/terpene alcohols in the different boron and ReTain® treatments of Goldrich apricot variety.

Figure 5.11a Effect of different treatments on volatile constituents of Orangered® Bhart

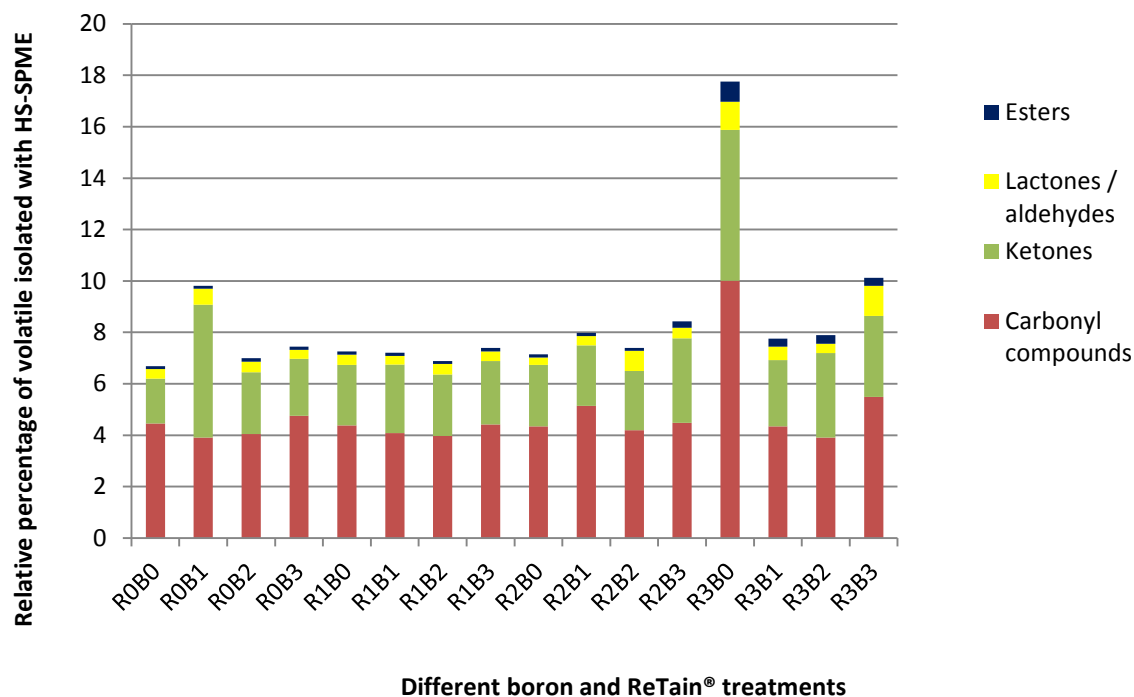


Figure 5.11a Relative proportions (percent) of the main classes of volatile compounds in the different boron and ReTain® treatments of Orangered® Bhart apricot variety. Concentrations of Treatments **Boron**: B0=1.2 Kg / ha, B1= 1.8 Kg/ ha, B2= 2.4 Kg/ ha, B3= 3.0 kg/ ha, **ReTain®**: R0= Water (control), R1 = 0.40 Kg/ ha, R2= 0.65 Kg/ ha, R3= 1.00 Kg/ ha.

Figure 5.11b Effect of different treatments on Terpenes / terpene alcohols of Orangered® Bhart

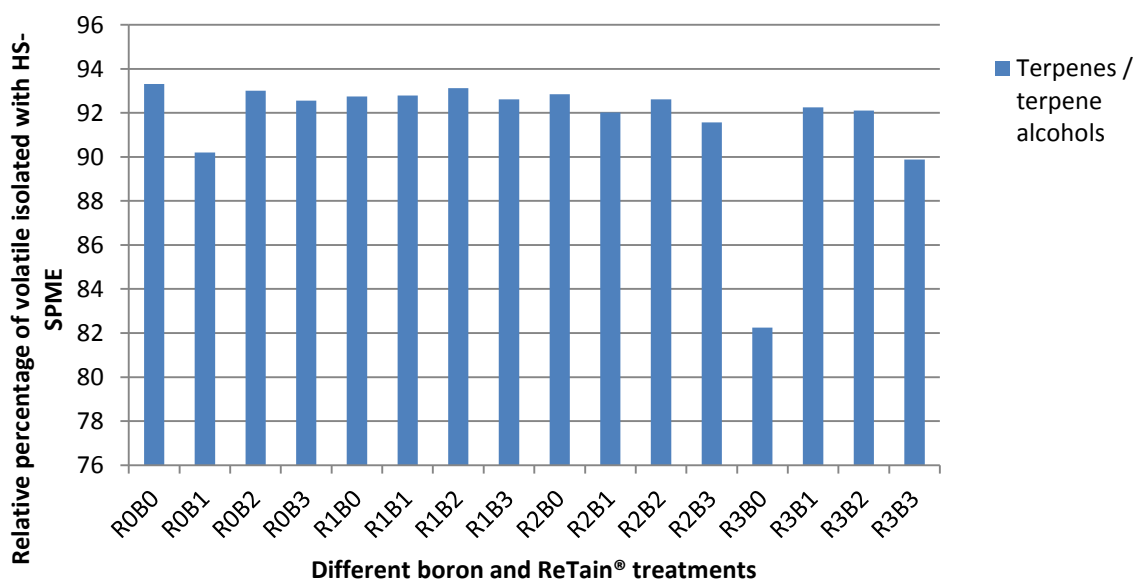
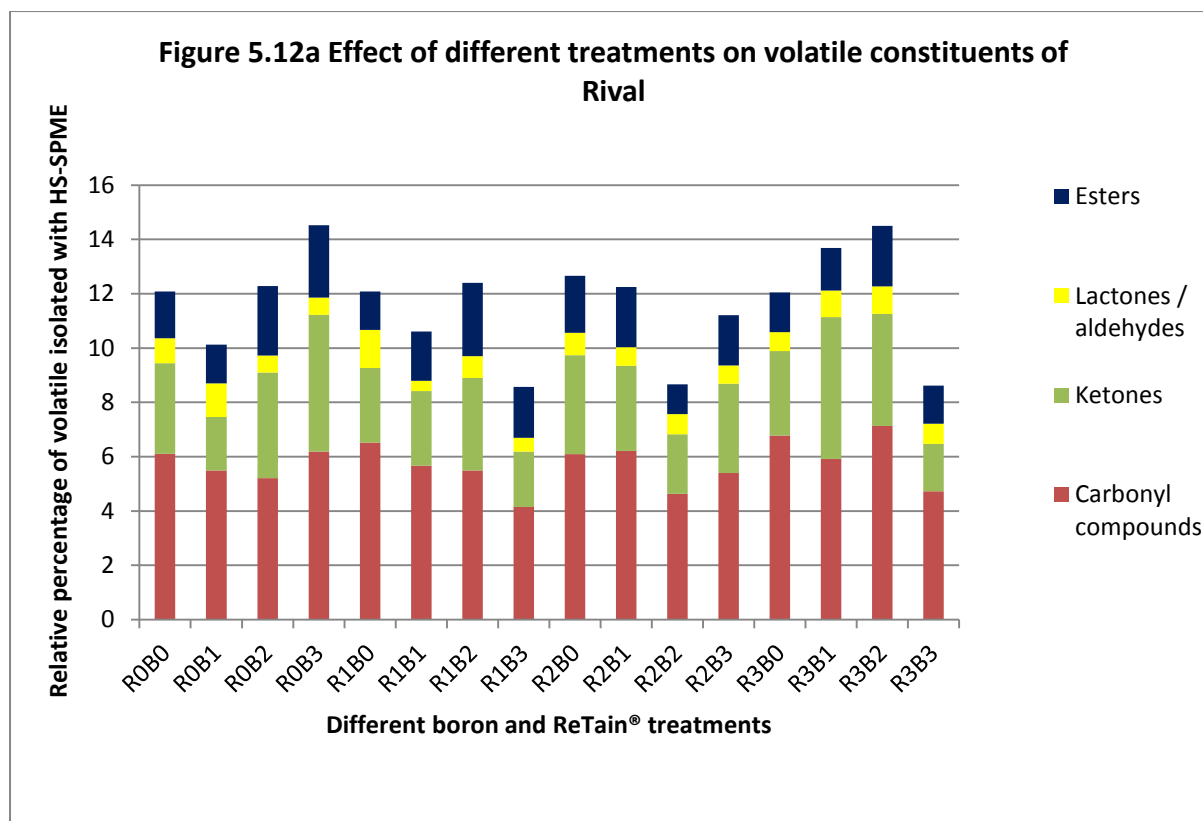
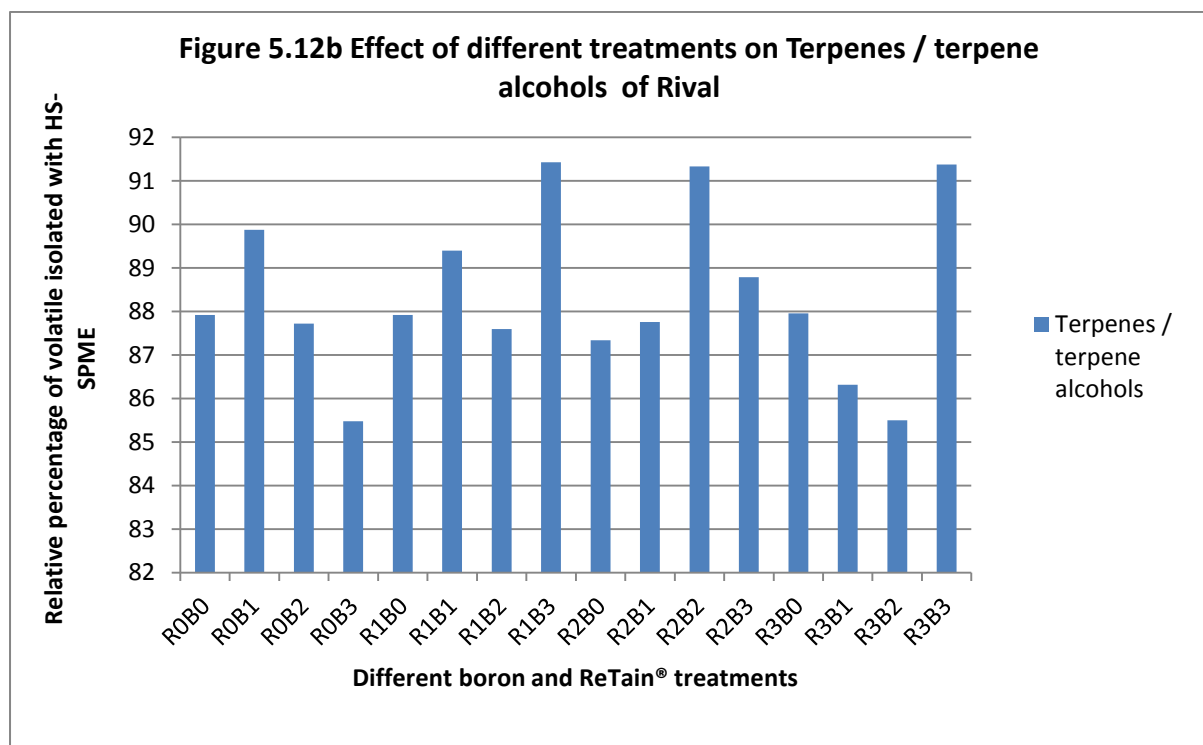


Figure 5.11b Relative proportions (percent) of terpenes/terpene alcohols in the different boron and ReTain® treatments of Orangered® Bhart apricot variety.





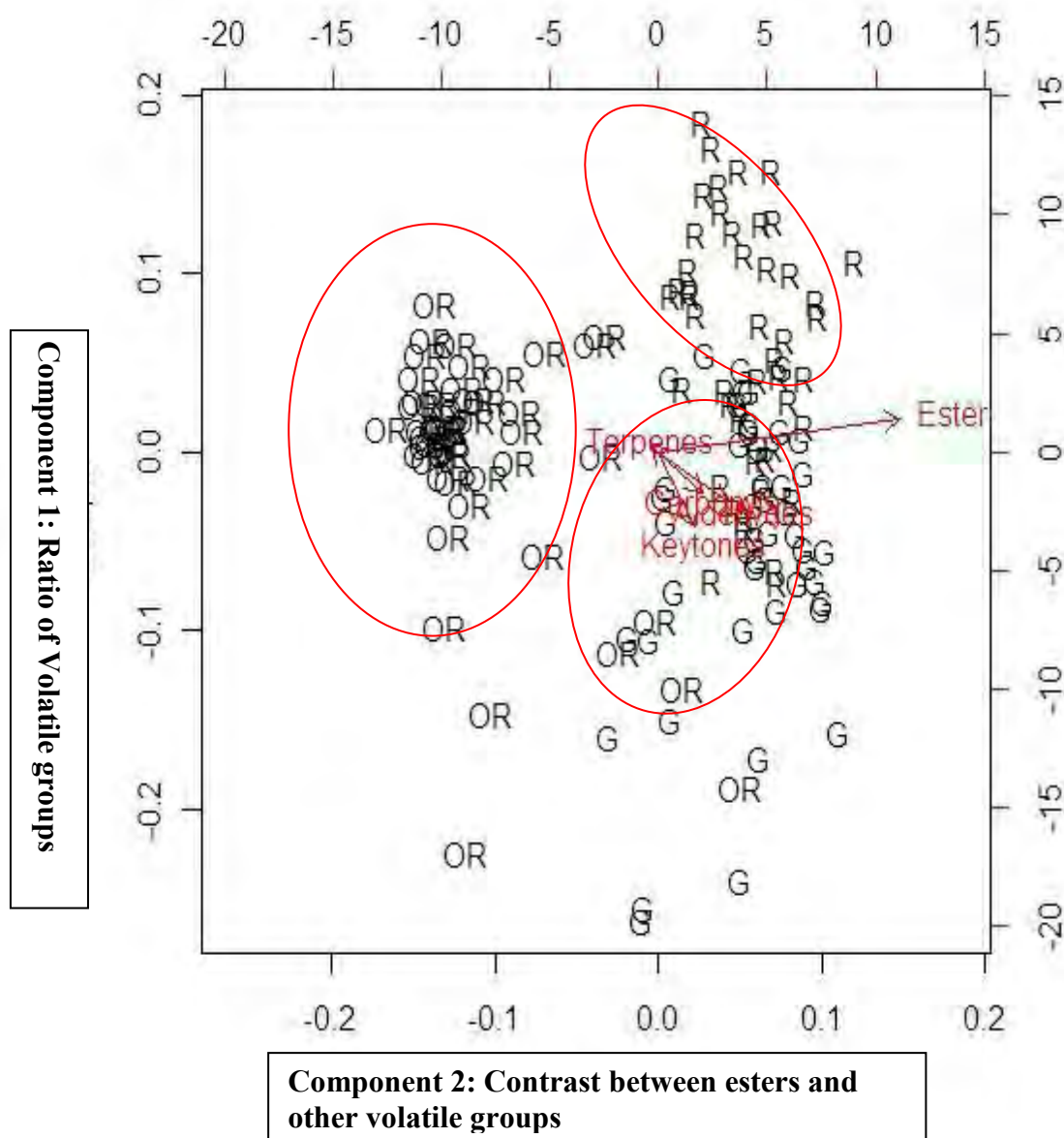
**Figure 5.12a** Relative proportions (percent) of the main classes of volatile compounds in the different boron and ReTain® treatments of Rival apricot variety. Concentrations of Treatments **Boron**: B0=1.2 Kg / ha, B1= 1.8 Kg/ ha, B2= 2.4 Kg/ ha, B3= 3.0 kg/ ha, **ReTain®**: R0= Water (control), R1 = 0.40 Kg/ ha, R2= 0.65 Kg/ ha, R3= 1.00 Kg/ ha.



**Figure 5.12b** Relative proportions (percent) of terpenes/terpene alcohols in the different boron and ReTain® treatments of Rival apricot variety. Concentrations of Treatments **Boron**: B0=1.2 Kg / ha, B1= 1.8 Kg/ ha, B2= 2.4 Kg/ ha, B3= 3.0 kg/ ha, **ReTain®**: R0= Water (control), R1 = 0.40 Kg/ ha, R2= 0.65 Kg/ ha, R3= 1.00 Kg/ ha.

<b>Table 5.11 Treatment P values of boron and ReTain® across 3 varieties and 4 boron and 4 ReTain® treatments with 3 replications.</b>				
<b>Treatment</b>	<b>Volatile group</b>	<b>Orangered® Bhart</b>	<b>Rival</b>	<b>Goldrich</b>
<b>Boron</b>	Ester	.040*	.420	.254
	Lactones	.065	.195	.003**
	Ketones	.802	.429	.000***
	Carbonyl	.000***	.103	.856
	Terpenes	.036*	.185	.001**
<b>ReTain®</b>	Ester	.000***	.555	.000***
	Lactones	.000***	.777	.000***
	Ketones	.260	.002**	.000***
	Carbonyl	.000***	.547	.000***
	Terpenes	.000***	.145	.000***
<b>Boron * Retain</b>	Ester	.001**	.159	.015*
	Lactones	.000***	.073	.042*
	Ketones	.144	.000***	.000***
	Carbonyl	.000***	.321	.045*
	Terpenes	.000***	.000***	.001**
<b><sup>b</sup> Concentrations mentioned in Table 5.3. * Low significant, **Moderately significant, *** Highly significant at <math>p&lt;0.000</math></b>				

The extraction of apricot VC by the SPME technique allows recovery of a range of volatile compounds as mentioned in Table 5.4. However, the single overall level of VC was not enough to differentiate among all three varieties across the different treatments. The differences in the concentration of individual groups of VC were a better determinant of the varieties and treatment effects. Each variety behaved significantly differently in terms of the boron and ReTain® treatment effects. However, there were major effects for all three varieties indicating considerable concern for apricot aromatic quality is needed when suggesting a new agronomic treatment. Across all groups of compounds and all treatments there was always at least one with a significant effect (Table 5.11). The combined treatments had significant effects on terpenes of all three varieties. Terpenes and terpene alcohols were significantly increased by ~12 % in Goldrich. There was a very small amount of increase (~0.45%) in Rival for terpenes and it slightly decreased in Orangered® Bhart.



**Figure 5.13 Results from PCA analysis (A) Projection of the samples of apricot dividing into three distinct groups of Rival(R), Goldrich(G) and Orangered® Bhart(OR).**

Figure 5.13 clearly indicates there are major differences between the varieties in the overall balance of VC though with some overlap arising from individual treatments. The proportion of the total variance explained by component 1 (0.2) and component 2 (0.2) is 0.4. The **component 1** in Figure 5.13 is the **Ratio of volatile groups** and the **component 2** is **contrasts between esters and other volatile groups**. Thus there may be benefits in the in orchard treatments to shift the balance among the VC compounds to make the variety more similar to another variety and hence improve its consumer perception. The differences also indicate that commercial varieties do not have the same VC composition giving the possibility of different consumer preferences, which will be tested in Chapter 6.

## 5.7 General discussion

The overall changes described in the results indicate comprehensive effects of variety and treatment on the volatiles contents of apricot. However, there has been little research on the specific content of individual volatiles in apricots so the above data can also be looked at in a very general way to see just what is present and what effects the compounds could have on the taste and smell associated with consumer acceptance of apricots. Therefore the discussion below looks at some of the individual compounds identified and what hedonistic effects they may have.

Aldehydes and alcohols are formed from acyl-CoA though the activity of acyl-CoA reductase and alcohol dehydrogenase, respectively (Bartley *et al.*, 1985). The unsaturated aliphatic aldehydes tend to produce stronger aromas. Benzaldehyde is reminiscent of bitter almonds and is associated with cherry flavor. The odour of citrus comes from aliphatic aldehydes as well as oxygenated terpenes like terpineol and citral.

$\gamma$ -decalactone has a more peach like fruity odour. This lactone is considered superior to Nonalactone ("Aldehyde C-18") and Undecalactone ("Aldehyde C-14") as a flavor material, and if it is of proper quality, it shows excellent versatility for substituting for part of one or both in combination fruit flavors where peach is the main theme, or where delicately fruity notes are desirable with sweet, mildly nut like or oily creamy flavor types. It is used in floral perfume, synthetic musk and in flavor compositions.

Dihydroactinidiolide and  $\beta$ -ionone can be regarded as carotenoid metabolism products (Ohloff, 1978). The mono terpene alcohols linalool,  $\alpha$ -terpineol, nerol and geraniol have been shown to exist in glycosidically bound forms in apricot (Salles *et al.*, 1988). Geraniol and nerol must exist predominantly in their bound forms as Guichard and Souty (1988) did not detect these compounds in apricot samples prepared under enzymic inhibition but found the glycosidically bound forms of the linalool oxides, benzyl alcohols and 2-phenylethanol. These compounds have been previously reported in apricot (Tang and Jennings, 1967). The present study found the listed volatiles giving good indications of their existence in glycosidically bound forms.

The esters play a role in the fruity odour. Though their concentrations were low, these values may not reflect their actual levels in the fruit. Alternative extraction methods need to be tested to determine the optimum method of extraction.  $\beta$ -ionone has been found as a major constituent (15.7%) in the essential oil of the blossoms of *Osmanthus fragrans* Lour (Sisido *et al.*, 1967). It has been reported in cassie (Demole *et al.*, 1969), raspberry (Winter and Enggist, 1971), passion fruit (Winter and Kloti, 1972), tea (Yamanishi *et al.*, 1973), artichoke (Kallio, 1976), and black chokeberry (Hirvi and Honkanen, 1985). It is, however, quite low in apricots according to this study.

Cymene is a constituent of a number of essential oils, most commonly the oil of cumin and thyme. Cymene is a common ligand for ruthenium. The parent compound is  $[(\eta^6\text{-cymene}) \text{RuCl}_2]_2$ . Cymene is prepared by the reaction of ruthenium trichloride with the terpene,  $\alpha$ -phellandrene. Terpenes such as 6-methyl-5-hepten-2-one have floral notes and have been described as resulting from degradation of lycopene (Drawert *et al.*, 1981), limonene has a citrus note and hexanal (0.07 – 2.7 ppm) a grassy note. It is important to understand that the actual active concentration of different compounds can be quite different so the relative importance may not follow the concentration in the fruit.

Limonene is a phytonutrient in a class of chemicals called terpenes. Major terpene producers are conifers such as pine, which produce it in resin. The word terpene is derived from the word turpentine. Terpenes contain isoprene units, which are a combination of 5 carbon atoms and 8 hydrogen atoms, and the different types of terpenes are classified according to how many of these isoprene units they contain.

Limonene is a monoterpene, meaning it has two isoprene units in its chemical makeup. It is a clear liquid whose molecules can come in two different types which are mirror images of each other. L-limonene has a piney turpentine like smell, and d-limonene smells like oranges. Thus it can have important quality effects on apricot and its presence there in substantial and a variable amounts (0.3 – 200 ppm) indicates it is an important variable in apricot aroma. It is used in some solvents in some model airplane gums and cleaners. However, d-Limonene is also a phytonutrient that can give important health benefits but the variable quantities found would be a major difficulty in promoting its benefits for apricots. As it is combustible, limonene has also been considered as biofuel.

Linalool (0.6 – 187 ppm) may be responsible for the floral character of apricots while the lactones provide the fruity, peach and coconut like back ground odour (Spencer *et al.*, 1978). However according to Arctander (1969) linalool has a light and refreshing, floral woody odour with a faintly citrusy note. It is used very extensively in perfume composition mostly of floral types and in oriental, amber, aldehydic, herbaceous and many other fragrance types. It is also used in blueberry imitation, lemon, lime, orange, grape, apricot, pineapple, black currant, plum, peach, cardamom and other spice complexes. It is also used in cocoa and chocolate imitation, as it gives pleasant effects with vanillin. In higher plants linalool, as well as other monoterpenoids are produced from isopentenyl pyrophosphate via the universal isoprenoid intermediate geranyl pyrophosphate, through a class of membrane-bound enzymes named monoterpene synthases.

$\alpha$ -terpineol can be present either free or conjugated. An increase in  $\alpha$ -terpineol due to the heat treatment in apricot pulp is reported by Chariote *et al.* (1981) which fits in with its presence partly in glycosidic form. Rhoades *et al.* (1972) showed that a mixture of nerol, geraniol,  $\gamma$ -decalactone,  $\alpha$ -terpineol and linalool added to freeze dried apricots gives a fresh, fruity flavor to the product.

Lactones are internally formed esters and in chemical equilibrium with their corresponding acids; 4 hydroxy acids transforms into  $\gamma$ -lactones and 5-hydroxy acids transforms into  $\delta$ -lactones. Lactones such as  $\gamma$ -decalactone were involved in the typical, basic apricot flavor whereas compounds like terpene alcohols such as linalool and  $\alpha$ -terpineol, ketones as and in some cases benzaldehyde were described as contributors of the flower and fruity notes of different apricot cultivars (Takeoka *et al.*, 1990). The information provided by Takeoka *et al.* is a matter of discussion because according to most viewpoints  $\beta$ -ionone (0 – 0.7 ppm in present studies) resembles cedar wood and has a raspberry like undertone while  $\alpha$ -ionone which is absent in apricots has a more typical violet odour, sweeter and less green than  $\beta$ -isomer (Arctander, 1969).  $\beta$ -ionone has industrial usages for the formation of Vitamin A and finds its way more into fragrances rich in woody notes and lipstick fragrances due to its raspberry note. It is used in its highest concentrations in Liquorice candy, chewing gum and as an imitation flavor component for Raspberry, strawberry, cherry etc.

Guichard and Souty (1988) sampled apricot volatiles under enzymic inhibition (ammonium sulphate) and identified 19 esters, 18 of which had not been previously reported in apricot. The esters have been the dominant constituents in the headspace sample in the studies of Takeoka *et al.* (1990). However, the results of our studies were contradictory to previous studies as terpenes and terpene alcohols were the dominant volatile constituents in all three apricot cultivars.

The production of esters in apricots is highly variable depending on the variety and normally increases during the maturation process (Botondi *et al.*, 2003; Aubert and Chanforan, 2007). A decrease was observed in the production of esters and aldehydes in the fruit applied with inhibitors, especially after 20 days at 0 °C in studies of Valdes *et al.* (2008) in apricots. These results suggest an effect of ethylene as a modulator of the biosynthesis of esters, a behaviour already studied in other climacteric fruits such as apple (*Malus domestica* Borkh.), melon (*Cucumis melo* L.) and papaya (*Vasconcellea pubescens* A. DC.)

In particular, d-limonene is used in large amounts for household product fragrances where the citrus odour is desirable or at least compatible with the product and purpose. It can be used with a multitude of fragrance types including floral types from Jasmine to Lavender bouquets and in Pine, aldehydic, woody, fruity or green odours (Arctander, 1969). The concentration of d-Limonene in the finished products is normally about 30-400 ppm except in chewing gum where it may be as high as 2300 ppm.

Myrcene has a sweet balsamic resinous gum odour. The commercial grades of myrcene contain 20 -25% of laevo-Limonene plus minor amounts of beta-Pinene and polymers. Apart from perfumery, this terpene finds use in citrus and spice colognes where its spicy balsamic and refreshingly light character introduces desirable notes. Myrcene is even used in masking odours for industrial purposes mainly because of its low cost. It is also used as component of artificial essential oils and as a fresh note in common household products.

However, with our studies the level of esters was not decreased by the treatments but they were always detected in very small quantities in all three varieties. Though increased by some treatments the highest level of esters in the VC was only ~ 3%. However, in a very small amount even this level was quite noticeable as esters play an important role in the fruity aroma of the apricot. The biggest increase might be the combined effect of boron and ReTain®. AVG is an active constituent of Retain® that could have suspended the production of esters for a time to delay the ripening process.

## **5.8 Conclusion**

Though the overall concentration of VC in Rival was greater than the other two varieties, the boron and ReTain® treatments had the least effects on this variety being significant in only 3 of 15 instances compared to 11 and 13 for Orangered® Bhart and Goldrich respectively. The ketones and terpenes significantly changed in Rival for the combined analysis. However, more research on volatiles needs to be done for treatment effects as these results were established only on the 30 identified volatiles from the SPME technique and will need more seasons of work to determine if there are general effects that are consistent across years.

All the five groups of volatile components i.e aldehydes/lactones, ketones, carbonyl compounds, terpenes and terpene alcohols, were at a maximum in the Rival variety. Rival could be well separated from the other two varieties in the PCA plot (Figure 5.13). As mentioned in 2.3.7.1 these compounds have been previously reported to be important in apricot aroma. Among them linalool, cymene and  $\alpha$ -terpineol were the main components in our samples.

It would be worth investigating consumer preferences for the different treatments to determine whether there is an association between hedonistic properties of the fruit as determined by trained/consumer panels and the levels of compounds found in the various treatments. A preliminary trial along these lines is included in Chapter 6.

The effect of changes in ethylene concentration, such as would be induced by ReTain®, on the development of aroma is complex, presenting a direct effect leading to the changes observed in esters and terpenes, concentrations while not having any effect on the level of alcohols and aldehydes. This situation shows the complexity of the fruit maturation process, in which it is established that ReTain® is only one factor among many other important factors (eg cultivar, maturity level) which determine VC level.

In conclusion this study has found that not only the type of cultivar but also the agronomical practices and environmental conditions affect the composition of important sensory compounds which is consistent with the results of Jirovetz *et al.*, (2003). The detailed analysis of changes in the aromatic profile of individual varieties due to treatment effects of boron and ReTain® provides a useful indication of overall fruit quality. Further investigations are needed to characterize these samples

from a sensory point of view (descriptive analysis, preference tests) in order to determine whether consumers are able or not to perceive differences between apricot varieties and effects of treatments. As a start on this approach consumer preferences were studied. A detail description of consumer analysis is given in Chapter 6.



## CHAPTER 6 CONSUMER PERCEPTION OF QUALITY FOR BORON AND ReTain® TREATED APRICOTS

### Abstract

Successful development of new rural industries depends on understanding and meeting consumer needs. A study was carried out to probe consumer understanding of apricot fruit quality and their perceptions of sensory attributes. The results were compared to instrumental measurements. A subset of the field experiment treatments was tested. These used three different varieties of apricot with either no extra boron or ReTain®, with added ReTain® or added boron and ReTain® making a total set of nine samples for tastings by representative consumers. Apricots were harvested at a similar maturity stage according to commercial practices. Analysis and sensory assessments were carried out on equivalent fruits from uniform samples.

Regression analysis was done between bulk samples (n=100), subset samples (n=30) and consumer perceived data. Despite the variability of response of assessors, significant differences were found between attributes of different treatments. Consumer preferences for most quality attributes correlated poorly with instrumental analysis. However, consumer perception of firmness correlated reasonably with instrumental analysis. Even though Goldrich is the firmest variety according to instrumental analysis, Orangered® Bhart sprayed with ReTain® scored highest for overall satisfaction according to consumer preferences. Untreated Orangered® Bhart had the highest average preference being ranked in the top three of nine different treatments for seven out of the eight assessments. These findings indicate that pre-harvest boron and ReTain® sprays can successfully increase apricot tree yields but have mixed results on fruit quality.

### 6.1 Introduction

Consumer satisfaction measurement is considered as the most reliable, feedback. It provides an effective, direct, meaningful and objective way of determining the customer's preferences and expectations. In this way, customer satisfaction is a baseline standard of performance and a possible standard of excellence for any business (Gerson, 1993). Domestic experiences need to be studied to identify constraints and recommendations to improve the post-harvest quality of apricot, reduce losses and promote products in domestic and foreign markets. The purposes behind such surveys are to develop minimum maturity standards that will assist the apricot industry to meet consumer's expectations.

Cultivar choices are important for consumer acceptance. The modern apricot industry needs commercial cultivars characterized by high fruit quality because too frequently consumers are not satisfied with the present quality standards of horticultural products. It is expected that the results of the surveys presented in this chapter will provide real, actionable information that can be used to drive decisions and performance in local orchards.

The health and nutritional benefit of apricot consumption is well documented in the literature review section. Understanding consumer perceptions and attitudes towards fruit quality is important in setting quality specifications for marketing as well as providing a useful guide for post-harvest research aimed at quality improvement of fresh apricots. The individual consumer has a set of preferences and values whose determinations are outside the realm of economics. The basic goals and standards that consumers strive to fulfill, including adherence to attitudes and beliefs held, are imbedded in the basic needs they strive to meet. These expectations refer to the fulfillment of functional needs (satisfaction), hedonic needs (enjoyment) or need for self-social identity through product use (Lundahl, 2006).

The acceptance or rejection of a food product will therefore be determined by the compatibility of food product attributes and consumer needs (Earle and Anderson, 2001). In our studies, fresh apricots can be formulated into a product that consumers desire, for example in the form of canned apricot or dried apricots. Food product attributes refer to the intrinsic or extrinsic characteristics that the consumer infers from the product and are therefore tangible properties that are measurable, manipulable and physically under the control of fruit growers (Van Kleef *et al.*, 2005). In this study, we investigate the frequency of fruit consumption and consumer perceptions of apricot quality with the help of self-administered questionnaires.

The yield and quality (Chapter 4) of apricots were manipulated and improved with the help of boron and ReTain® foliar sprays in the orchard. Pre-harvest foliar sprays were used for boron application and the plant growth regulator ReTain® was sprayed on at different stages of development of the apricot fruits. The different treatments gave significant effects as discussed in Chapter 4 and Chapter 5. However, these results do not provide the complete analysis as it is the final consumer who will determine whether a practice has value or not. A research survey was conducted in the form of a questionnaire to understand consumer perception for the boron and ReTain® treatment effects. Questionnaires have advantages over some other types of surveys in that they are cheap, do not require as much effort from the questioner as verbal or telephone surveys, and often have standardized answers that make it simple to compile data.

Sensory testing is necessary to help growers and orchardist appeal to the conscious and unconscious preferences of consumers that enhances the repeated buying habits of consumers. Such testing is commonly used nowadays to evaluate fruit quality. Frequently, trained panels can draw up the profile of the fruit and provide an accurate description. However, the main drawback is the high costs in terms of time and money and the difficulty to assess simultaneously a large number of samples. As a result most of the studies incorporate a combination of trained panels and normal consumers to analyze the preferences of consumer behavior.

Consumer panels, trained sensory panels and instrumental analysis can be used to help guarantee that a product's quality is consistent from batch to batch. It is very important to understand the need of the consumers and their preferences towards apricots before the application of laboratory based research into the market. To determine these attitudes for apricots from our boron and ReTain® trials a short research survey in the form of a questionnaire regarding preferences and attitudes of consumers towards apricots was undertaken. The questionnaire was divided into three main parts.

### **Part 1: Personal Information about the consumer**

This part of the questionnaire collected data about the consumers, their attitudes and their eating and buying habits, thereby providing useful background information for an apricot marketing strategy.

### **Part 2: Consumer preferences for quality of apricots**

Consumers are always looking for good quality and tasteful fruit and would be happy to pay more for that. On the other hand, growers are being pushed by retailers to produce fruit that has a longer shelf-life and looks attractive to consumers. Taste is not often one of the retailers' requirements for fruit to be sold to consumers.

Consumers have told us loudly and clearly that flavor is paramount in the enjoyment of food (Dr. Beauchamp, 1999, Washington USDA Conference). Growers normally do not have enough technical information on how to produce and deliver high-flavor fruit to consumers. The quality of fruit diminishes after harvest if it is not delivered in good time or handled and stored properly. This part of the questionnaire will explore the desired preferences of consumers for the quality of apricots. It will analyze the form of apricots consumers desire (canned, dried, fresh or processed from) and their ideas about quality attributes. It will even categorize the most important quality parameters of apricots according to consumer's choices. Descriptive techniques are used to generate quantitative data that describe similarities and differences among a set of products.

### **Part 3: Consumer perceptions of different quality attributes of apricot**

Supply chains in new and emerging agricultural industries typically lack information linking product quality with consumer behavior. Assessing and modeling consumer response to product quality provides information that demonstrates to supply chain stakeholders how better product quality management can improve the performance of the whole chain.

The boron and ReTain® treated samples were used to identify the preferences of the consumer. It is important to identify the preferences of the consumers for boron and ReTain® treated apricots. The emerging fruit industries, therefore, have more incentive to adopt a supply chain orientation if they understand quality-related factors that drive consumer satisfaction and repeat buying behavior.

The main aims of this research survey were thus:

- 1.) To provide consumers with good quality apricots produced by means of sustainable agricultural practices based on their needs.
- 2.) To identify possible links between sensory data and instrumental data for different boron and ReTain® treatments on apricots for better understanding of the apricot quality characteristics.
- 3.) To provide farmers, wholesalers and retailers of the apricot industry with information on how to produce quality fruit with a probability of obtaining higher prices for good quality fruit.

## **6.2 Materials and Methods**

Selection of the samples to use for consumer testing were done from four different treatments of boron and four different treatments of ReTain® for three varieties of apricots namely Rival, Goldrich and Orangered® Bhart. As there were a total of 16 different treatments for each variety in the study, it was not possible to evaluate all treatments. Therefore, selections of three treatments for all three varieties making a total of nine treatments were used in the survey. These spanned the maximum ranges of treatments i.e. minimum boron and no ReTain® (R0B0), maximum boron and maximum ReTain® (R3B3) and maximum ReTain® and minimum boron (R3B0) for three varieties namely Rival, Goldrich and Orangered® Bhart.

### **6.2.1 Difference test**

The difference test method was a duo-trio test (O'Mahony, 1979). Each consumer was presented with three apricot samples, each consisting of two pieces. The three samples were a labeled reference sample and two coded samples. The reference sample and one of the coded samples were taken from the same fruit, while the other coded sample was from a different fruit. The participant's task was to taste the slices and indicate which coded sample was the same as the reference. The same test was repeated thrice with the same candidate. If the participant successfully identified the two different samples at least twice from three tests, they qualified for the complete survey. Consumers who failed to reach this standard were eliminated. This step was crucial for selection of consumers as it was important for the study to have participants who had a good idea about quality parameters of apricots.

Before the commencement of the survey, ethics approval was obtained from the Human Research Ethics Committee of the University of Tasmania. The survey was conducted at a private function room to maintain the standard procedures necessary for the survey. From the total 100 selected participants 25 were trained panelists and the other 75 were consumers. Consumer panelists consisted of people visiting the sites where the sampling was done. A table with signs and a description of the work was used to inform people of the purpose; as they approached the table they were asked if they were interested in participating in the panels. These judges had no previous training in sensory evaluation work.

The trained panelists were either from the fresh fruit industries or people having previous experience of taking part in sensory studies of different fruits. Ten of the trained panelists were from Coles or Woolworths and 15 were from the University academic and research staff. Most of the staff members that participated had previous knowledge of perennial fruits and some of them had detailed knowledge of sensory studies. The experiment was divided into 10 batches. Each batch consisted of 10 participants. A total of 10 batches of consumers participated in the questionnaire. The participation was entirely voluntary.

Each participant was provided with an individual table and chair. Apricot samples were cut into small pieces by a qualified chef and served into nine different bowls then were presented to each consumer. The bowls were arranged randomly and each bowl was given a specific numeric label. The survey was done under standard light conditions. Participants were asked to taste each fruit sample and provide ratings for overall liking. Carbonated water was used to cleanse the palate. Sufficient time was allowed for palate recovery before each assessment.

The participant tasted the apricot fruit from the 9 different bowls placed in front of them and filled out a questionnaire regarding their preferences and attitudes towards apricots. Before analysis fruits were kept at room temperature until they reached full maturity.

### **6.2.2 Design of questionnaire**

The final form of questionnaire is presented in Appendix 3. There are a number of different testing protocols that can be followed for consumer testing. In hedonic testing, a consumer is presented with the apricot samples and asked to evaluate each of several different samples on a number of different fruit quality parameters. It is customary in hedonic testing to have the test subject rate from a low value (e.g. extreme dislike) to a high value e.g. (liked extremely). The hedonic data should be considered with caution though, as one of the principles of sensory evaluation is that a descriptive panel should adopt an analytical frame of mind and set aside personal preferences and hedonic reactions (Lawless and Heymann, 1999; O'Mahony, 1979).

The first part of the questionnaire used in this study gave a basic idea about buying habits of consumers and necessary information required to assess the reliability, generalizability and source credentials of the collected data. The second part of questionnaire dealt with six different quality parameters namely color, firmness, sweetness, acidity, flavor and overall satisfaction. The reliability of the assessment was enhanced by the initial difference test. In addition to evaluating the individual qualities, the participants were asked to provide a Likert scale rating indicating how well he or she liked the overall apricot quality i.e. taking into account all quality factors which the participants were asked to evaluate.

Likert scales for hedonic testing typically require a response from 1 to 3, 1 to 5, 1 to 7, or 1 to 9. Frequently larger scales may be reduced post hoc to 1 to 3 scales (good; neutral; bad) to simplify analysis. We generally used a 1 to 4 response factor because initial testing indicated that selection of a wide scale with responses of 1 to 9 exceeded the panelist's ability to distinguish categories. With 1 to 4 response factor, 4 indicated that the consumer is least enamored by the specific quality and 1 indicated the most important quality preference of the consumer.

To confirm the preferences the same questions were asked in a reverse style where ranking of the quality parameters were given from 1 (extreme dislike) to 4 (most liked) quality attributes. This forced slightly different thought process so that the question responses were independently developed.

Some of the tastings were done through forced choice testing i.e., the consumers were forced to choose between two apricot samples. In certain situations, it is not possible or feasible to conduct forced choice testing, e.g., when the apricot flavors are so strong that tasting for more than two products, or tasting the products a second time to select a preference, is precluded. Alternatively, time limitations may be such that adding the task of additional forced choice comparisons among all combinations of samples is unreasonable and/or excessive. Thus, in such situations, it may be difficult to obtain meaningful forced choice data. Once all respondents had been tested, forced choice preferences were determined. Finally the average overall-liking score for each sample (the sum of all respondents' overall-liking scores for a given product divided by the total number of respondents) was calculated.

The nine different samples given to consumers were selected combinations of treatments on which instrumental analyses were also performed. There were three combinations of Goldrich, three of Rival and three of Orangered® Bhart varieties. The combinations used are listed in Table 6.1.

<b>Table 6.1 Treatments used in the consumer survey</b>			
	<b>Rival</b>	<b>Goldrich</b>	<b>Orangered® Bhart</b>
Control	RR0B0	GR0B0	ORR0B0
Maximum ReTain®	RR3B0	GR3B0	ORR3B0
Maximum boron and ReTain®	RR3B3	GR3B3	ORR3B3
Concentration of Boron: B0=1.2 Kg B/ ha, B3= 3.0 kg/B ha ReTain® R0= Water (control), R3= 1.00 Kg/ ha R- Rival, G-Goldrich and OR-Orangered® Bhart.			

A field pilot test of the questionnaire was conducted during 20-24 December 2009 and a total of 32 interviews were completed. These 32 trial interviews are not included in the analysis. As a result of the pilot a small number of questions were changed and several pre-codes were added to the answer lists. This was just a trial of the final experiment which was performed in 2010. It is the final questionnaire used for the main stage of the fieldwork that can be seen in Appendix 3. Both the pilot and final questionnaires were approved by the University of Tasmania human ethics committee prior to use.

### **6.2.3 Instrumental analysis**

The physical and chemical determinations conducted on these treatments were for: soluble solid contents (SCC), titrable acidity (TA), visual color analysis, fresh weight, volume, firmness and qualitative analysis of volatiles with HS SPME. For each batch of 10 consumers three samples were tested in the laboratory to have a subset of samples making a total of (n=30) samples.

The methods involved to process the treated apricots are described in Chapter 3 in detail. The results for the original bulk samples of 16 different treatments (n= 108) are discussed in Chapter 4.

These data were compared by regression analyses with appropriate consumer preference tests to determine if there was a convincing relationship and whether it was possible to determine the optimal laboratory value for growers to target. This would generally be where the consumer test gave a value of '0' by the scale system used.

### **6.2.4 Statistical analysis**

Data were analyzed using the general linear models procedure (PROC GLM) of the Statistical Analysis System (SAS Institute Inc, Cary, North Carolina) where appropriate. The GLM procedure used the method of least squares to fit the general linear models. Average quality characteristics were calculated for the effects of treatments. The effect of different boron and ReTain® treatments on the quality parameters such as flavor, size, color, sugar, acidity, ripeness and overall satisfaction was tested. The significance tests are based on a 99% confidence interval with the General Linear Model.

In order to determine the probability of obtaining the given result on the null hypothesis, results were used with significance evaluated at 95% confidence or  $\alpha = 0.05$ . For the preference tests descriptive statistics were used to determine the percentages of subjects in various subcategories. Preference test results were evaluated for significance using Pearson chi square tests evaluated at 95% confidence to determine whether two nominal variables were unrelated.

Category data were analyzed using the Chi square method with Graphpad® Instat 3 software (GraphPad software Inc.). Overall liking scores were compared using paired *t*-tests and evaluated for significant difference at 95% confidence intervals. Analysis of Variance (ANOVA) was performed on individual scores using SAS procedure GLM to test the quality parameters of different treatments.



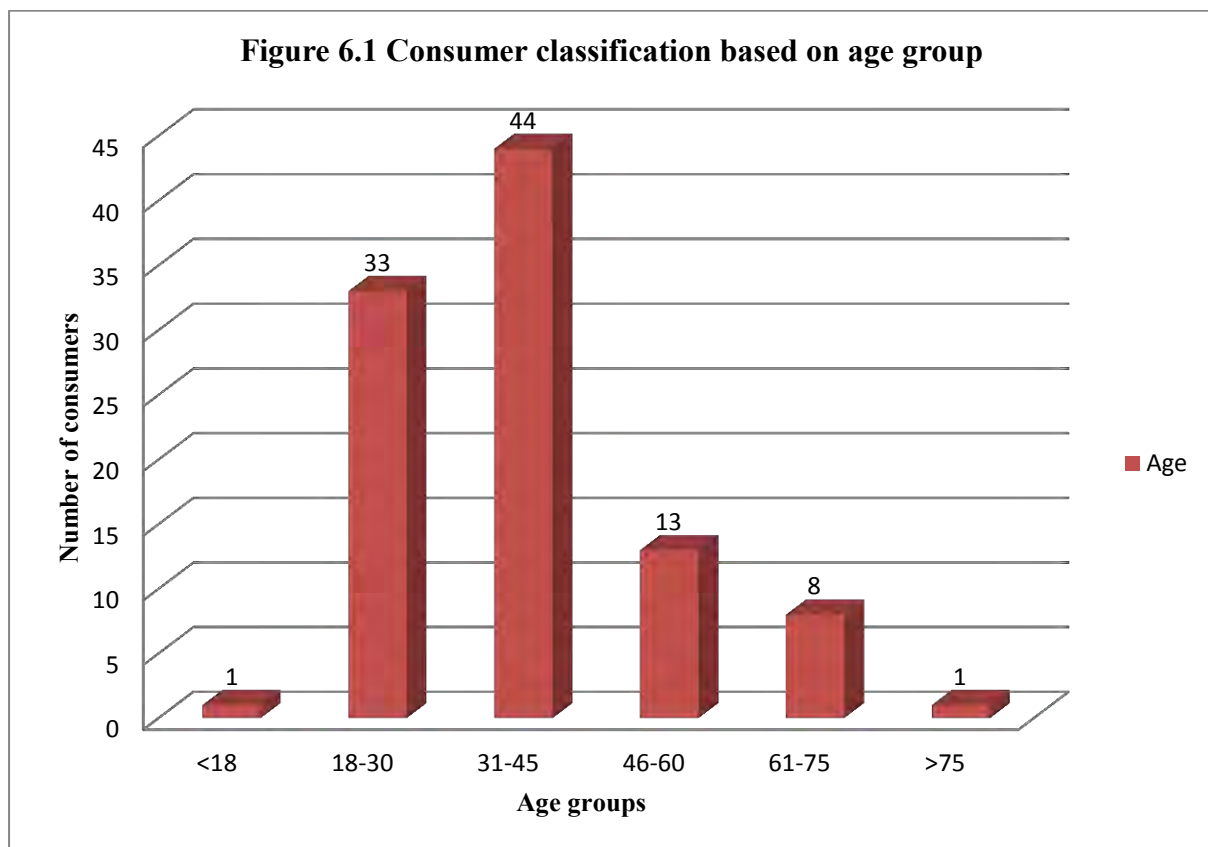
Linear regressions were conducted using Microsoft Excel® to establish relationship between the analytical measures associated with a particular sensory attribute or fruit characteristic and the corresponding rating or hedonic assessment.

## 6.3 Results and Discussion: Consumer characteristics

### 6.3.1 Classification of consumer groups based on innate characteristics

Demographic factors such as household size and age distribution of the population can alter consumption trends for fruit and vegetables (USDA, SB-928). This has been extensively investigated in Brisbane by Winkler (2008). Knowing the profile of potential customers is very important for marketing purposes since managers could maximize their advertising efforts and resources by targeting the right population.

The majority of respondents (44 %) were at least 45 years old, with 33 % in the 18-30 age bracket and 9 % in the 61 or older category age group. About 13 % fell in the 18-30 age brackets; and only 1 % was less than 18 years (Figure 6.1). With regards to gender, as expected, about half of the population sampled (53 %) were women ( $\chi^2=0.36$ ,  $P=0.55$ ) and the difference was not significant.



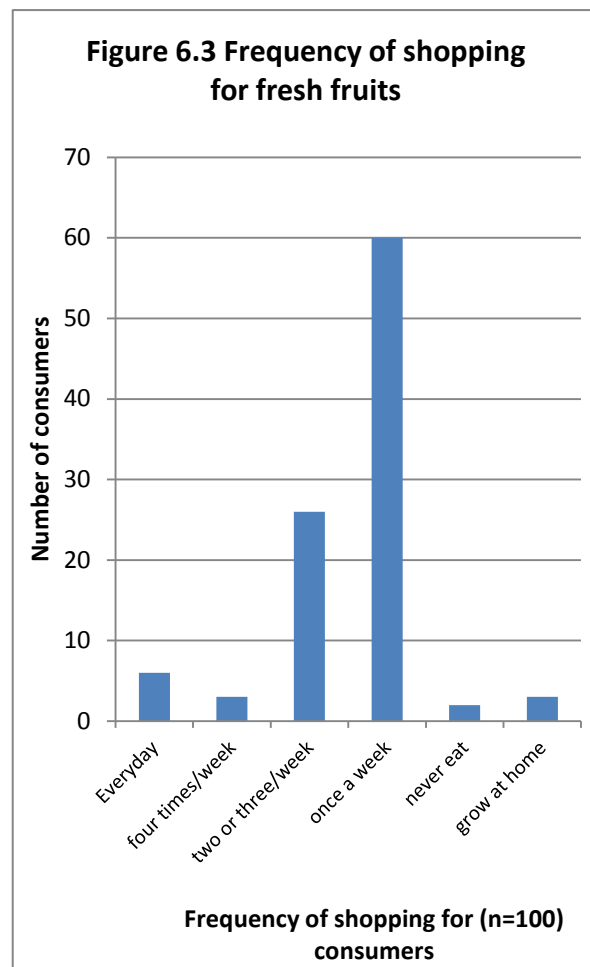
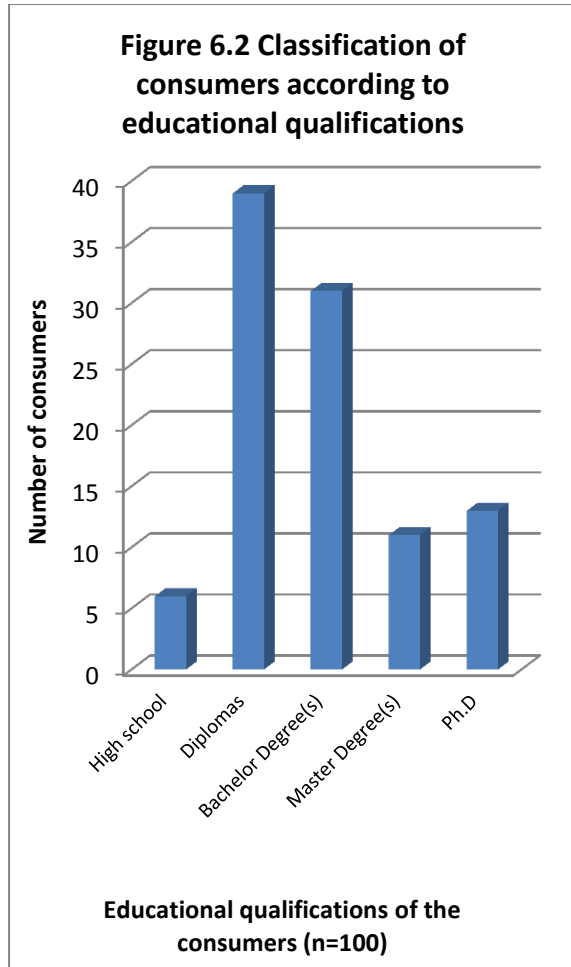
**Table 6.2 Age categories and percentage of the 100 participants in each group**

Age group	Male (47 %)	Female (53 %)
Less than 18 years	2 %	0 %
18 – 30 years	15 %	17 %
31 – 45 years	16 %	28 %
46 – 60 years	6 %	6 %
61 – 75 years	7 %	2 %
Above 75 years	1 %	0 %

**\*Distribution of ages among male and female not significantly different ( $\chi^2=8.8$ ,  $P=0.11$ )**

The maximum number of the males and females who participated in the survey was in the age group of 31-45 years followed by 18-30 years. There were no females less than 18 years or above 75 years who participated in the survey.

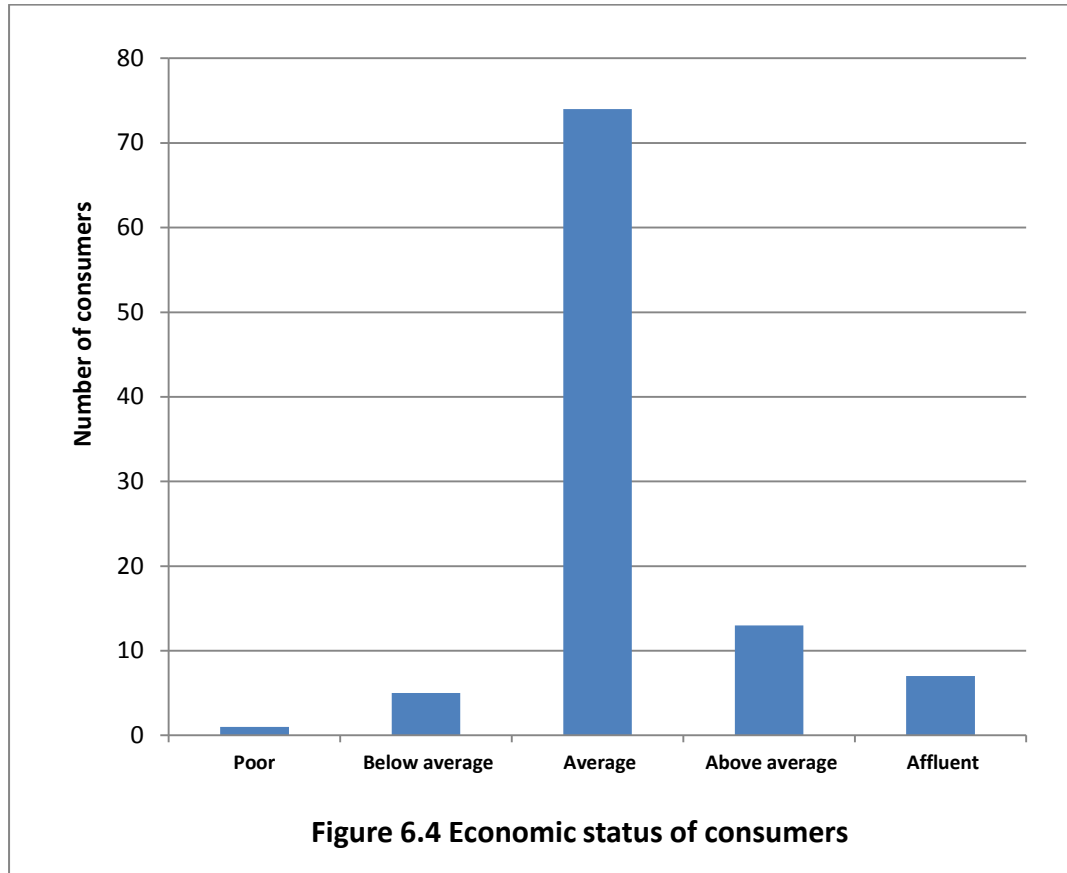
It was very important to have information about the educational qualifications of the consumers. Anova and chi square test ( $\chi^2=49.42$ ,  $p<0.0001$ ) indicated a significant relationship between educational qualification and economic status of the consumers in these studies. Logically the higher frequency fruit consumers tend to have above average to affluent economic status. This data indicates that they will also have better formal qualifications. This consumer group will have higher expenditures on fruits per capita as well as consumption of better quality (more expensive) and a wider assortment of fruits.



Of the tested consumers 39 % had educational qualifications up to diploma level (Figure 6.2). 30 % consumers had completed bachelors and 10 % had completed their master degrees. Twelve % of the consumers had completed higher research degrees. Most of these sections of consumers were the researchers from the university who were a major part of the trained panel. There was a significant relationship ( $\chi^2=71$ ,  $p<0.0001$ ) between educational qualification and buying habits (frequency of shopping) of the consumers.

With respect to how frequently consumers shop for fresh fruit, approximately 60 % of the 100 respondents said once a week; 24 % indicated twice or thrice in a week and 6 % purchased fruits every day. The differences in buying habits of the consumers was not uniformly distributed with  $\chi^2= 61.02$  and  $p<0.0001$ . From the daily purchase 6 %, 3 % were young women who were dieting and the remaining 3 % were older people with weak teeth who found it difficult to chew other options of available food (Figure 6.3). Only 2 % grew apricots at home though most of the consumers had gardens at their homes and 1 % never ate fresh fruits. These results seem to be generally in accordance with other studies of fruit and vegetable purchase behavior (Winkler 2008).

### 6.3.2 Classification of consumer groups based on economic factors



A consumer's economic status plays an important role in influencing their purchasing behavior. We cannot expect an individual operating under poor economic conditions to purchase fresh fruits twice/thrice in a week due to the cost. Most of the consumers who had average income were frequent shoppers for fresh fruits. Table 6.3 shows the relationship between these two different parameters of the consumers that affects the buying habits of the consumers.

However, relationships between income and shopping behavior were not clear from this project as 72 % of the consumers in the survey had average economic status and only 6% had below average economic status. Specific financial figures were not set in the survey to avoid embarrassment of the consumer so situations were self-reported estimates. In the trial survey of 2009, financial figures were set and most of the information provided contradicts the original identification of the consumer. To avoid these sorts of issues, in the final questionnaire the figures were not set. 24 % of the consumers earned above average and 6% were below average. Only 7 % were affluent. There were only 1 % of consumers who reported themselves as poor.

**Table 6.3 Relationship between economic status and buying habits of consumers.**

Status	Everyday	Four times a week	Twice/three times a week	Once a week	Never eat fruit	Grow fruit at home
Poor	0	0	0	0	1	0
Below average	0	0	3	2	0	0
Average	3	3	18	42	2	2
Above average	0	0	4	13	0	0
Affluent	0	0	3	3	0	1

A significant relationship ( $p=0.032$ ) was established between the economic status and buying habits of the consumers with ANOVA. A comparison of consumers who had fruit once per week or less against 3 groups of consumers (above average: average: below average) did not give a significant chi square value. Diet quality is affected not only by age and sex, but also by occupation, education, and income levels or social class (Turrell *et al.*, 2001, Winkler, 2008).

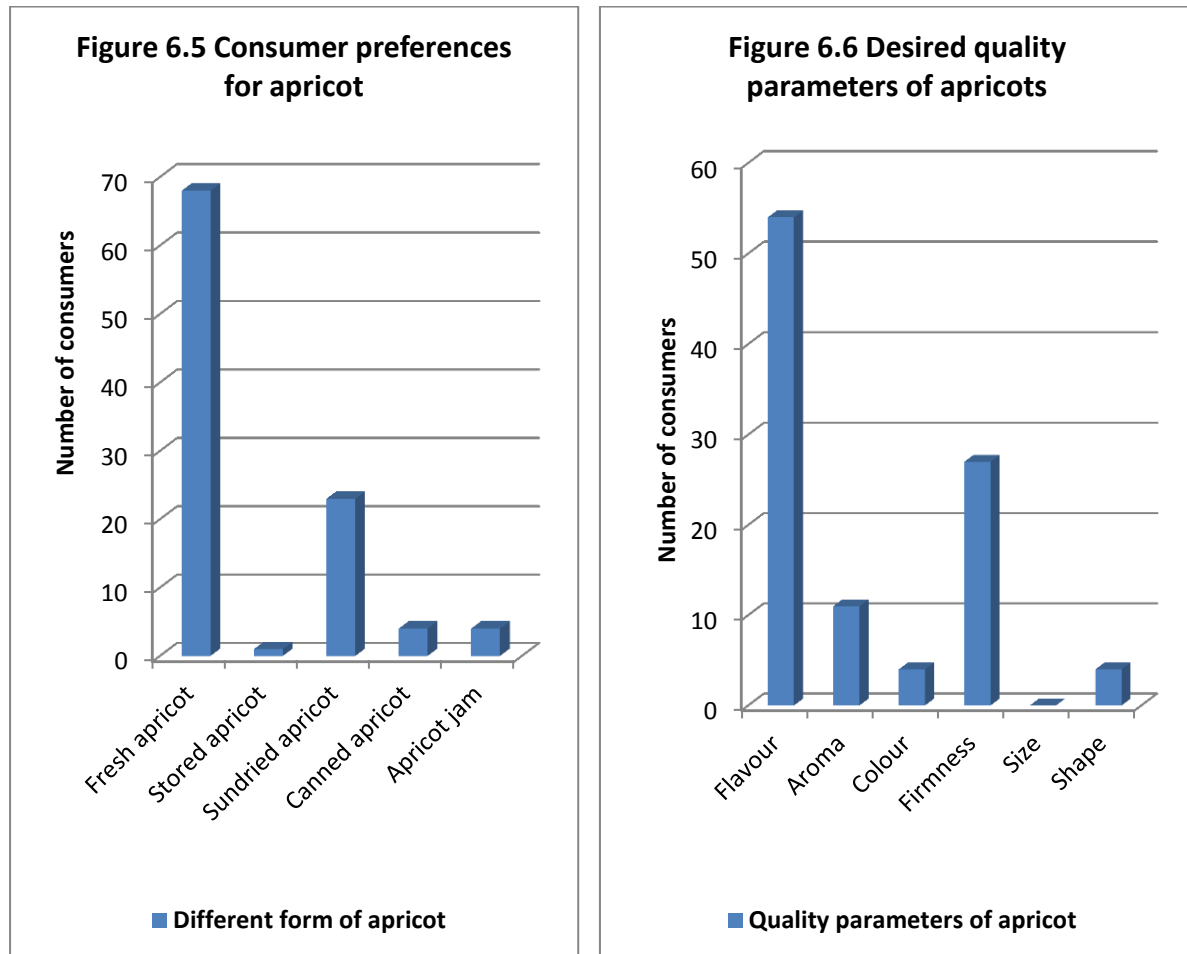
Assessing both education and occupation, improves the description of social class inequalities in dietary habits, as they act, most of the time, as independent factors (Galobardes *et al.*, 2001). Consumers with average and above average income were the main purchaser of fresh fruits. However, all the below average income consumers purchased fresh fruit at least once in a week.

The analysis had similar trends to those given by the Australian Bureau of Statistics, 2009 that depicts the income of different people in Australia. Nearly 68% of Australians had a near average annual income according to the data. This might be the reason why more than 75 % of the participants were either in average or above average income groups. These data suggest a need for further research using a larger more targeted group selection to determine among different income groups the reasons that consumers in different categories are avoiding consumption of fresh fruits.

### 6.3.3 Consumer preferences for quality parameters

This study provides an overview of attitudes, preferences and characteristics of consumers for consumption of apricots. Besides demographics, the characteristics examined in this survey include consumption trend of apricots, preference for quality parameters and frequency of visits. The results are based on a consumer survey of 100 consumers, from which 25 were trained panelists.

As shown in Figure 6.5, on average consumers preferred fresh apricots, followed by sun dried apricots. All forms of apricot were not equally preferred with significant differences among consumers for consumption (among fresh apricot: dried apricot: processed apricot;  $\chi^2=59.2$ ,  $p<0.0001$ ). The consumption of apricot jam and canned apricot was the same and stored i.e. frozen apricots were the least preferred form of apricot. This suggests expansion of the period of availability of fresh fruit would be an important need for consumers. There were 74 % of consumers who reported themselves from urban areas and 26 % were from rural area.



Survey participants were asked to rate the most important quality characteristics required in fruit (Figure 6.6). Significant differences existed among consumers in what they considered the most important character ( $\chi^2=89.9$ ,  $p<0.0001$ ). This means not all characteristics were preferred by the same proportion of the participants.

More than 50 % of consumers thought flavor to be the most important characteristic of apricot. As most of the participants were from urban area with access to multiple markets and diverse fruits, they have tasted more than a few varieties of apricots.

Taste was selected as the most important criteria for apricots. The lack of firm apricots with high availability in local super markets made consumers choose firmness as the second most important quality characteristic of apricots. 25 % of consumers prefer firm fruit so that they can store the fresh apricot for a long time and consume it 3-4 days after shopping. These were followed by aroma at 10 %. Consumers were generally not worried about size, though 4 % of consumers were interested in shape of the apricots and 4 % had a specific preference for color of the apricots. This was contradictory to the expected outcomes as logically the consumers buy fruits while perceiving the color and aroma that defines the ripeness of the fruit. Thus consumers are forced to infer flavor from physical and visual status in the shops. This suggests that if a direct flavor test was available (i.e. taste sampling) consumers would have better congruence between desired and available purchase information and may increase purchase behavior.

The insights provided by this survey are expected to help producers and managers of the Tasmanian apricot market to allocate their resources more efficiently to better meet consumers' needs. Moreover, consumer's demographic and socio-economic characteristics could aid marketers in the identification of potential target markets.

**Table 6.4 Chi Squared values for paired comparisons of 3 varieties of apricots across 3 ReTain®/boron treatments for 8 consumer (n=100) rated quality parameters for three different apricot varieties. Scoring values are listed in Table 6.6.**

Perceived quality parameters of apricots	Different varieties of apricots	Chi Square values			Mean
		Goldrich	Rival	Orangered® Bhart	
Size	Orangered® Bhart	320.42*			-0.11
	Goldrich		167.87*		0.6
	Rival			93.73*	0.21
Color	Orangered® Bhart	155.6*			0.34
	Goldrich		18.08*		-0.25
	Rival			96.82*	-0.11
Brix	Orangered® Bhart	60.27*			-0.09
	Goldrich		28.81*		-0.33
	Rival			117.34*	-0.48
Acidity	Orangered® Bhart	91.49*			-0.04
	Goldrich		3.72 <sup>n.s.</sup>		0.33
	Rival			113.28*	0.37
Firmness	Orangered® Bhart	9.38*			0.14
	Goldrich		22.88*		0.28
	Rival			53.72*	0.49
Flavor	Orangered® Bhart	45.22*			0.05
	Goldrich		39.11*		-0.28
	Rival			134.71*	-0.53
Ripeness	Orangered® Bhart	25.97*			-0.11
	Goldrich		61.53*		-0.26
	Rival			136.55*	-0.55
Overall Satisfaction	Orangered® Bhart	47.06*			0.03
	Goldrich		38.07*		-0.3
	Rival			121.35*	-0.54
Chi Squared values followed by *are highly significant with a significance level at $p < 0.001$ . Scoring values are listed in Table 6.6. ReTain®/boron treatments are Listed in Table 6.1					



**Table 6.5 Chi Squared values for paired comparisons of 9 different boron and ReTain® treatments of apricots. Consumer (n=100) rated eight quality parameters across three different apricot varieties.**

Perceived quality parameters of apricots	Different treatments of apricots	Chi Square			Mean
		R3B3	ROB0	R3B0	
Size	ROB0	52.35*			0.29
	R3B0		17.66*		0.36
	R3B3			54.09*	0.05
Color	ROB0	19.02*			-0.16
	R3B0		45.45*		0.12
	R3B3			8.42*	0.02
Brix	ROB0	44.89*			-0.25
	R3B0		6.44 <sup>n.s.</sup>		-0.32
	R3B3			24.03*	-0.34
Acidity	ROB0	9.17 <sup>n.s.</sup>			0.19
	R3B0		0.15 <sup>n.s.</sup>		0.17
	R3B3			10.62 <sup>n.s.</sup>	0.29
Firmness	ROB0	38.89*			0.13
	R3B0		21.69*		0.35
	R3B3			3.64 <sup>n.s.</sup>	0.43
Flavor	ROB0	43.06*			-0.19
	R3B0		26.05*		-0.24
	R3B3			5.79 <sup>n.s.</sup>	-0.32
Ripeness	ROB0	33.29*			-0.20
	R3B0		5.98 <sup>n.s.</sup>		-0.29
	R3B3			14.35*	-0.42
Overall Satisfaction	ROB0	53.74*			-0.26
	R3B0		29.08*		-0.25
	R3B3			4.97 <sup>n.s.</sup>	-0.29

Chi Squared values followed by \*are highly significant with a significance level at  $p < 0.001$ . n.s. = Not significant

Scoring values are listed in Table 6.6.

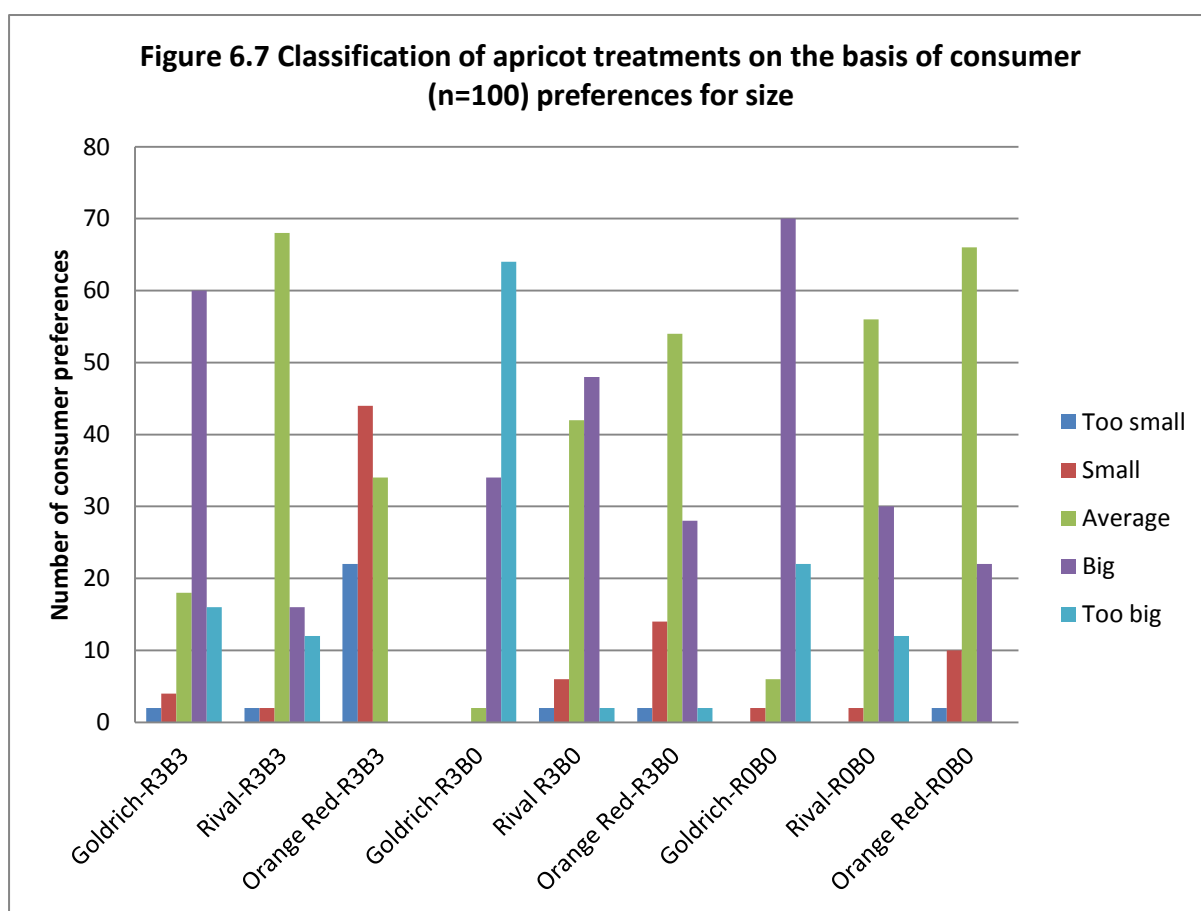
ReTain®/boron treatments are Listed in Table 6.1

## 6.4 Results and Discussion: Consumers perceptions of the different treatment samples of apricots for individual quality characters

Tables 6.4 and 6.5 summarize the  $\chi^2$  values and significance for paired comparisons of the treatments across varieties and ReTain® /boron applications. The next sections look more closely at the interaction tables for the quality characteristics.

### 6.4.1 Consumer perception of apricot samples for fruit size

Consumers rated each sample using a 5 point scale (Too small, small, average, big and too big) where the participants were instructed to rate each sample relative to their individual notion of ideal size of apricots for personal consumption. The results were analyzed by coding them as -1 was too small, -0.5 was small, 0 was average, 0.5 was big and 1 was too big. Zero (0) was kept as average as it is the most desired characteristic value. Based on the weighted average scores were Goldrich=0.60; Rival=0.21; Orangered® Bhart =-0.11; R3B3=0.05; R3B0=0.36; and R0B0=0.29 (Table 6.4; Figure 6.7). This suggests that the maximum boron and ReTain® application produces the most average size fruits as preferred by consumers.



A  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived size distribution among the 3 varieties ( $\chi^2$  is equal to 167, 93 and 320 for G: R, R: OR and OR: G respectively). More importantly  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived size distribution among the 3 treatments across varieties ( $\chi^2$  is equal to 54, 18 and 52 for comparisons of R3B3:R3B0, R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5. With the perceived size analysis, participants were not willing to accept a slightly smaller fruit as ideal fruit.

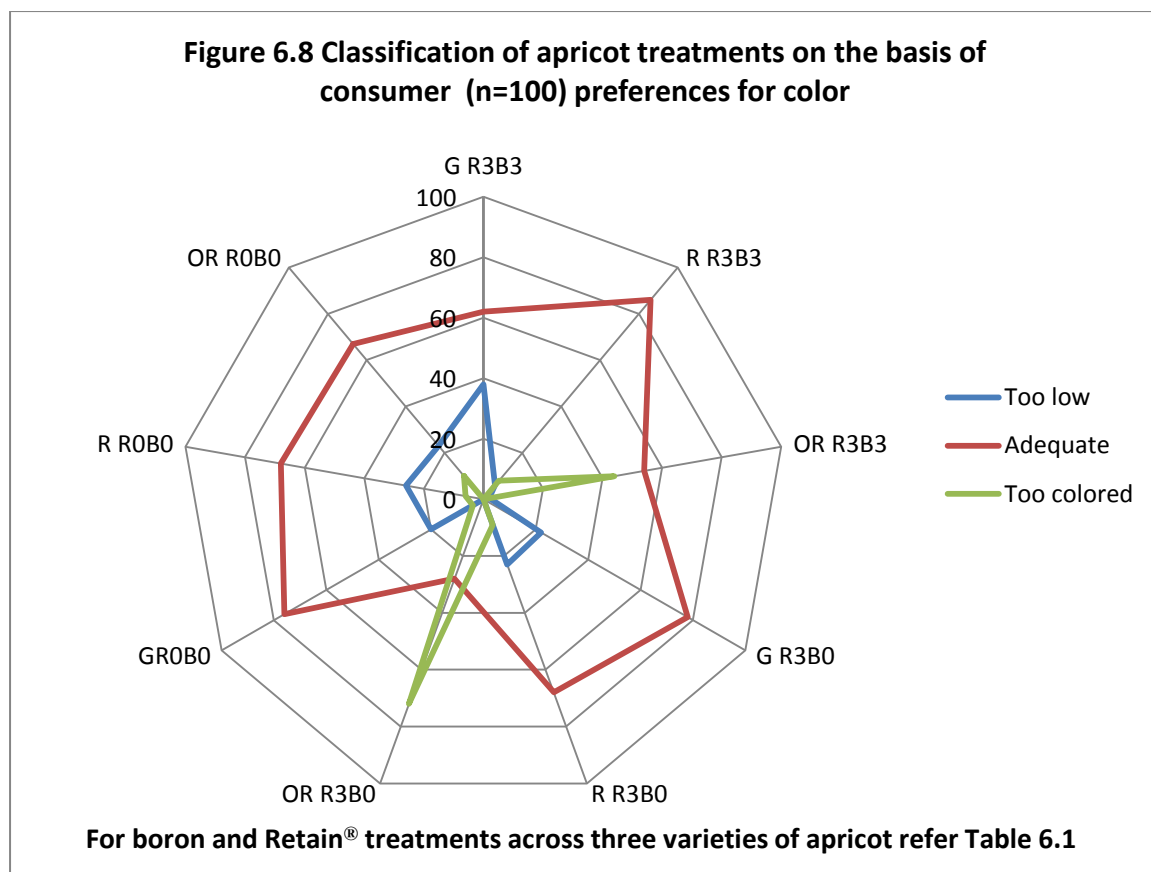
For all treatments except OR R3B3 “average”, “big” or “too big” accounted for 84-100% of consumer ratings. For OR R3B3 66% of participants found OR R3B3 had below average size fruits. The regression equations given in Table 6.7 suggest the optimum fruit size was ~110 g. This value was calculated based on the regression equation value where the perception value was 0. The relationships between the factors of gender, participant age and educational qualifications on the size preferences of apricots were non-significant ( $p > 0.05$ ).

#### **6.4.2 Consumer perception of apricot samples for skin color**

To pursue trends in consumer preferences, a visual color analysis was done. A color scale was developed in relation to how the color was seen. Consumers rated each sample on a 3 point scale (Too low, adequate and too colored). They were instructed to rate each sample relative to their individual notion of the ideal color of apricots.

The results were analyzed by coding them as -1 for too low colored, 0 for average and 1 for too colored. To make reliable visual evaluations, multiple variables such as the spectral quality, intensity and angular size of the light source, the direction from which the light struck the apricots, the direction in which the sample was viewed and the distance between the viewer and the sample were controlled.

When the data were examined for influences of other characteristics there was a significant relationship found (p value 0.074 at 99% confidence intervals) between the color perception of Goldrich R3B3 (0.006 at  $p < 0.0001$ ) and Goldrich R0B0 (0.074 at  $p < 0.0001$ ) in a comparison of female and male responses

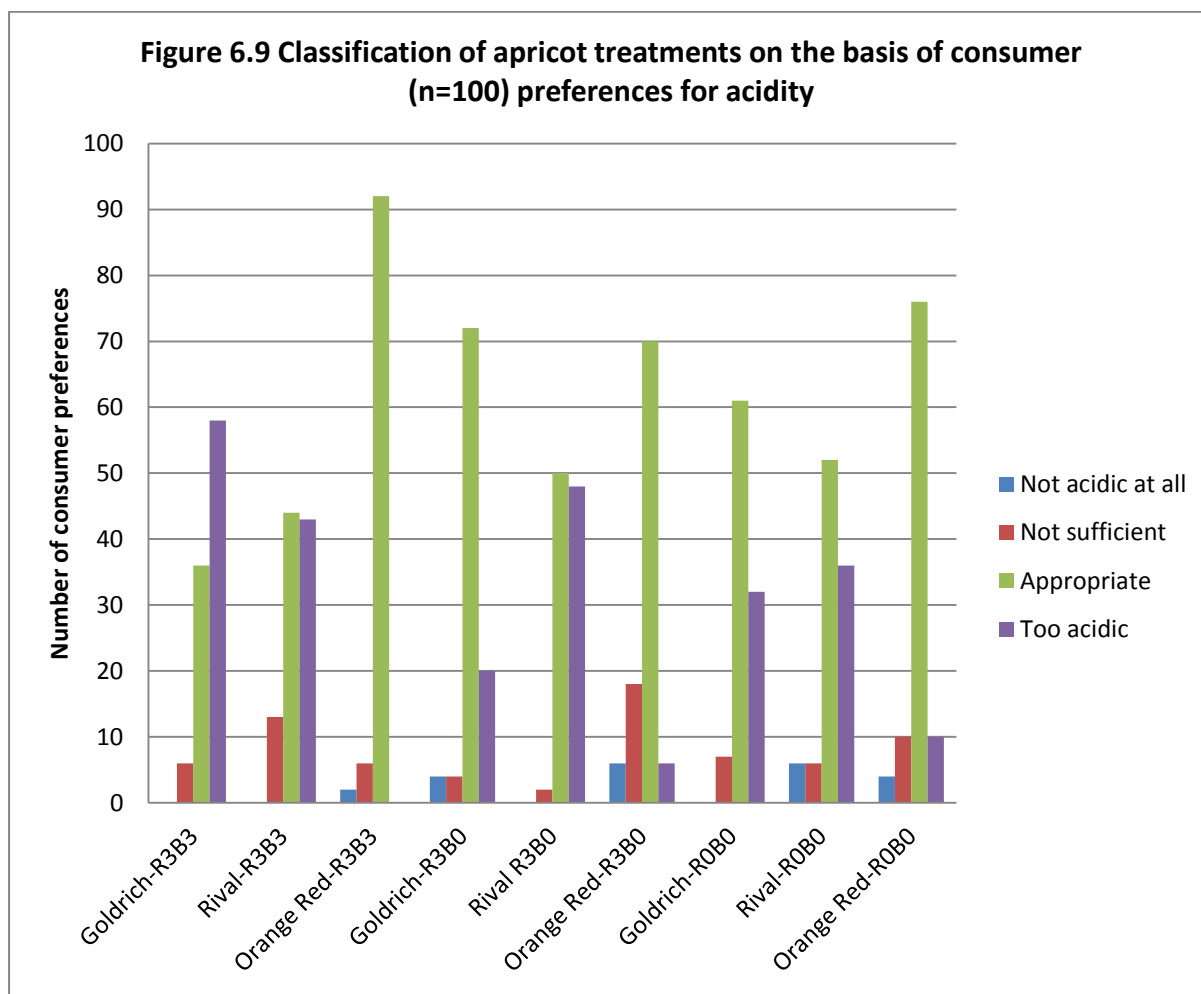


Based on the weighted average scores were; Goldrich=-0.25; Rival= -0.11; Orangered® Bhart =0.34; R3B3=0.02; R3B0=0.12; and R0B0=-0.16 (Table 6.4 and 6.5). These scores suggested that the combination of high boron and ReTain® application produced the best colored fruit. As illustrated in Figure 6.8, 67 % of consumers rated R3B3 treated apricots as adequately colored compared with 58% for R3B0 and 70% for R0B0 treated apricots suggesting that though ReTain® improved firmness of apricots, there is little clear effect on the proportion perceiving adequate color.

However, a  $\chi^2$  comparison of too colored for the R3 treatments against the R0 treatments indicated that ReTain® significantly increased ( $\chi^2=34$ ;  $p<0.0001$ ) the proportion of too colored (6.7% to 22.2%) apricots in the sample. The color of the Rival and Goldrich was appreciated by 74 and 72 % of the consumers respectively. This was more so than Orangered® Bhart where 42% found it too colored.

A  $\chi^2$  analysis showed that there were significant differences ( $p<0.0001$ ) in perceived color distribution among the 3 varieties ( $\chi^2$  is equal to 18, 96 and 155 for G: R, R: OR and OR: G respectively). More importantly  $\chi^2$  analysis showed that there were significant differences ( $p<0.0001$ ) in perceived color distribution among the 3 treatments across varieties ( $\chi^2$  is equal to 8.4, 45 and 19 for R3B3:R3B0, R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5.

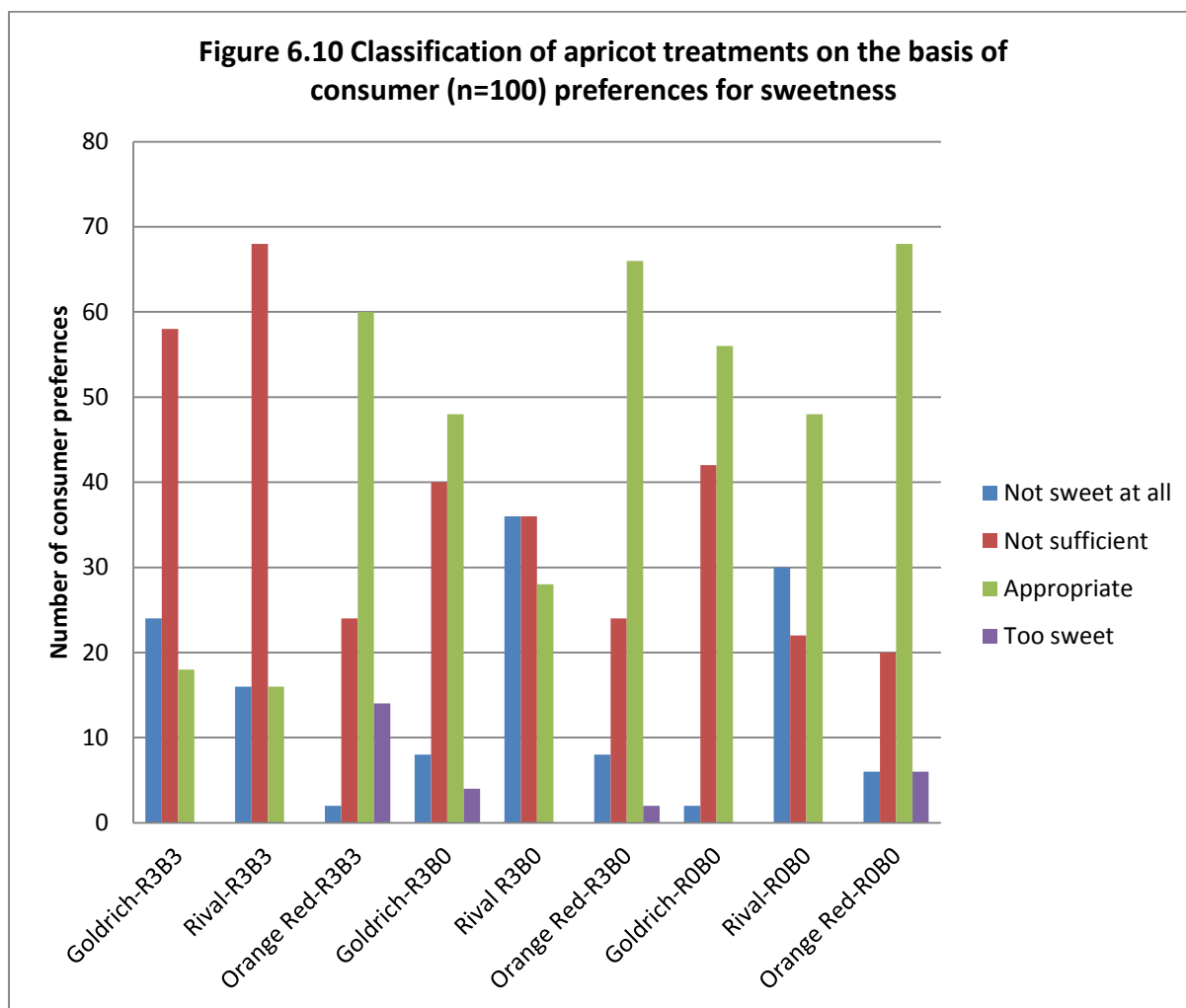
### 6.4.3 Consumer perception of apricot samples for acidity



Consumers rated each sample on a 4 point scale (Not acidic at all, not sufficient, appropriate and too acidic) where they were instructed to rate each sample relative to their individual notion of ideal acidity or sourness of apricots. The results were analyzed by coding them as -1 for not acidic at all, -0.5 for not sufficient, 0 for appropriate and 1 for too acidic. Based on the weighted average scores were; Goldrich=0.33; Rival=0.37; Orangered® Bhart = -0.04; R3B3=0.29; R3B0=0.17; and R0B0=0.19 which suggests the lower boron application and Orangered® Bhart produced more acidic fruit. 79% of consumers found appropriate acidity of Orangered® Bhart variety while 42% consumers perceived Rival to be most acidic in taste giving a sour flavor. 33% of consumers found R3B3 treatment produced too acidic fruits and 64% consumers found R3B0 treatment produced appropriate acidity.

The  $\chi^2$  analysis showed that there were significant differences in perceived acidity distribution among the 3 varieties (Table 6.4). More importantly  $\chi^2$  analysis showed that there were significant differences in perceived acidity distribution among the 3 treatments across varieties as shown in Table 6.5.

#### 6.4.4 Consumer perception of apricot samples for sweetness



Consumers rated each sample on a 4 point scale (not sweet at all, not sufficient, appropriate and too sweet) where they were instructed to rate each sample relative to their individual notion of ideal sweetness of apricots. The results were analyzed by coding them as -1 for not sweet at all, -0.5 for not sufficient, 0 for appropriate and 1 for too sweet. The rating of not sufficient was added to the final set to analyze the preferences in detail as the trial set indicated it was needed.

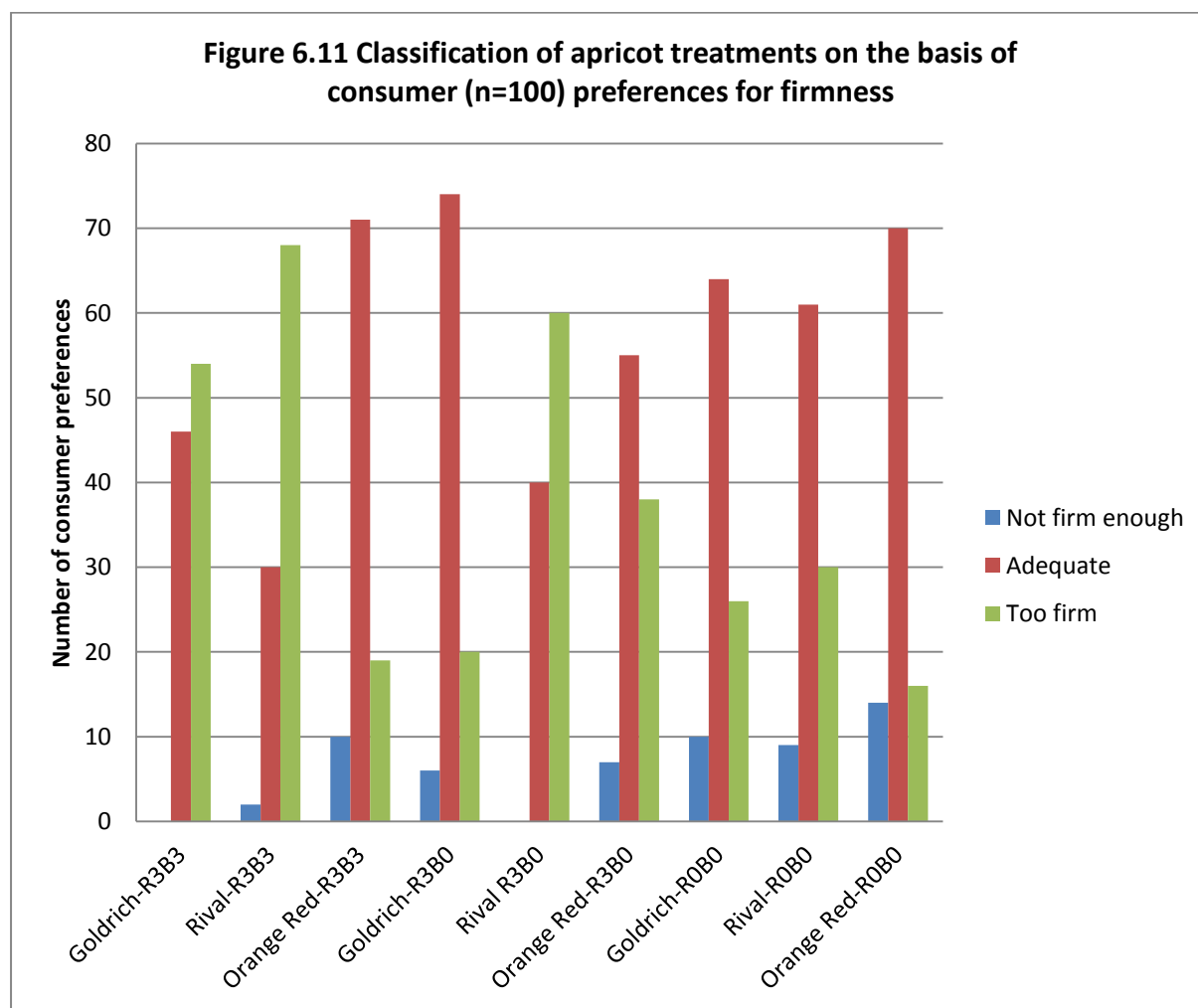
Based on the weighed average scores were; Goldrich=-0.33; Rival=-0.48; Orangered® Bhart = -0.09; R3B3=-0.34; R3B0=-0.32; and R0B0=-0.25 which suggests that maximum ReTain® treatments decreased the sweetness of the apricots slightly with little effect of added boron. Orangered® Bhart was the most preferred variety with 65% of consumers ranking it as appropriate compared with Goldrich (41%) and Rival (31%) in terms of sweetness. Seven percent of consumers perceived Orangered® Bhart as over ripe fruits. Goldrich and Rival were considered to be highly lacking in sweetness by ~11 and 27% of the consumers respectively compared with 5% for Orangered® Bhart. 14% of consumers rated

R3B3 treated apricots as not sweet, 17 % rated R3B0 treated apricots as not sweet at all and 13% rated R0B0 in the same category. R3B3 treatments gives fruitful result on Goldrich and Rival variety, however there is no treatment effect on Orangered® Bhart according to the consumer perception.

A  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived sweetness distribution among the 3 varieties ( $\chi^2$  is equal to 28, 117 and 60 for G: R, R: OR and OR: G respectively). More importantly  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived sweetness distribution among the 3 treatments across varieties ( $\chi^2$  is equal to 24, 6.4 and 44 for R3B3:R3B0, R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5.

#### 6.4.5 Consumer perception of apricot samples for firmness

Consumers rated each sample on a 3 point scale (not firm enough, adequate and too firm) where they were instructed to rate each sample relative to their individual notion of ideal firmness of apricots. The results were analyzed by coding them as -1 for not firm enough, 0 for average and 1 for too firm apricots.



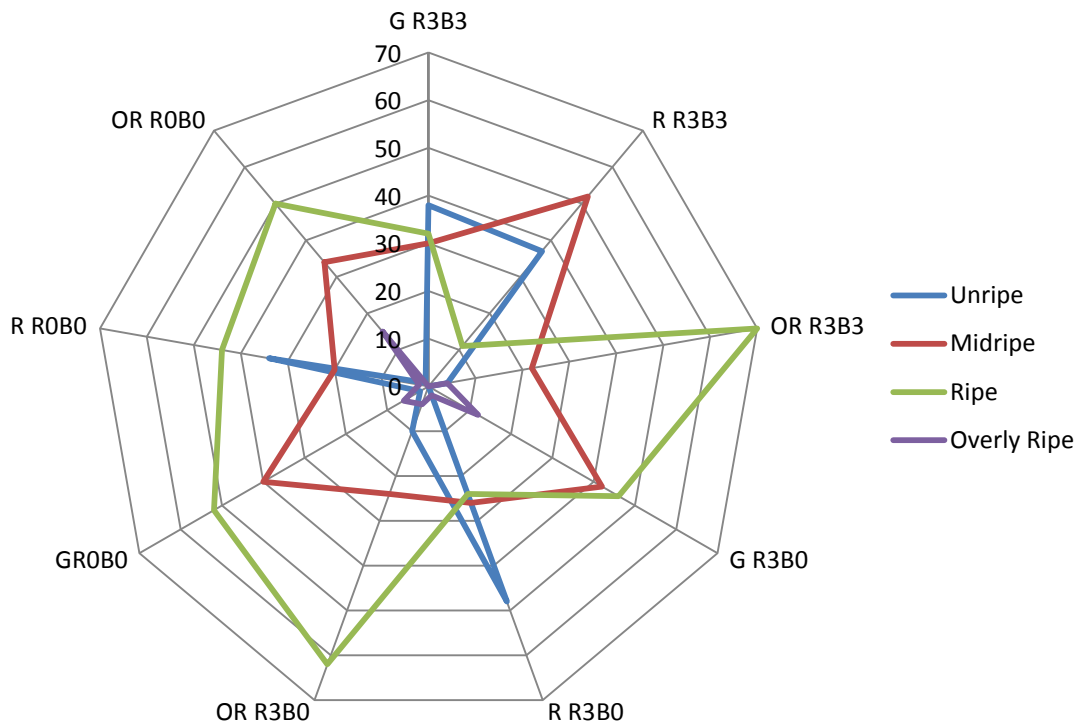
Based on the weighted average scores were; Goldrich=0.28; Rival=-0.49; Orangered® Bhart = 0.14; R3B3=0.43; R3B0=0.35; and R0B0=0.13 which suggests that maximum ReTain® and boron treatment increased the firmness of the apricots.

A  $\chi^2$  analysis showed that there were significant differences ( $p<0.0001$ ) in perceived firmness among the 3 varieties ( $\chi^2$  is equal to 22, 53 and 9.3 for G: R, R: OR and OR: G respectively). More importantly  $\chi^2$  analysis also showed that there were significant differences ( $p<0.0001$ ) in perceived firmness for two treatments across varieties ( $\chi^2$  is equal to 45 and 19 for R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5 and Figure 6.11.

Orangered® Bhart was the most preferred variety in terms of firmness with 65% of consumers rating it adequate, followed by Goldrich (61%) and Rival (44%). 53% of consumers perceived Rival as too firm. 56% of consumers rated R3B0 treated apricots to be adequately firm and 47% of the consumers rated R3B3 treated apricots as too firm.

#### 6.4.6 Consumer perception of apricot samples for ripeness

**Figure 6.12 Classification of apricot treatments on the basis of consumer (n=100) preferences for ripeness**



For boron and Retain® treatments across three varieties of apricot refer Table 6.1



Consumers rated each sample among four different ripeness options (Unripe, midripe, ripe and overly ripe) where they were instructed to rate each sample relative to their individual notion of ideal ripeness of apricots. The results were analyzed by coding them as -1 for unripe, -0.5 for mid ripe, 0 for average and 1 for overly ripe apricots.

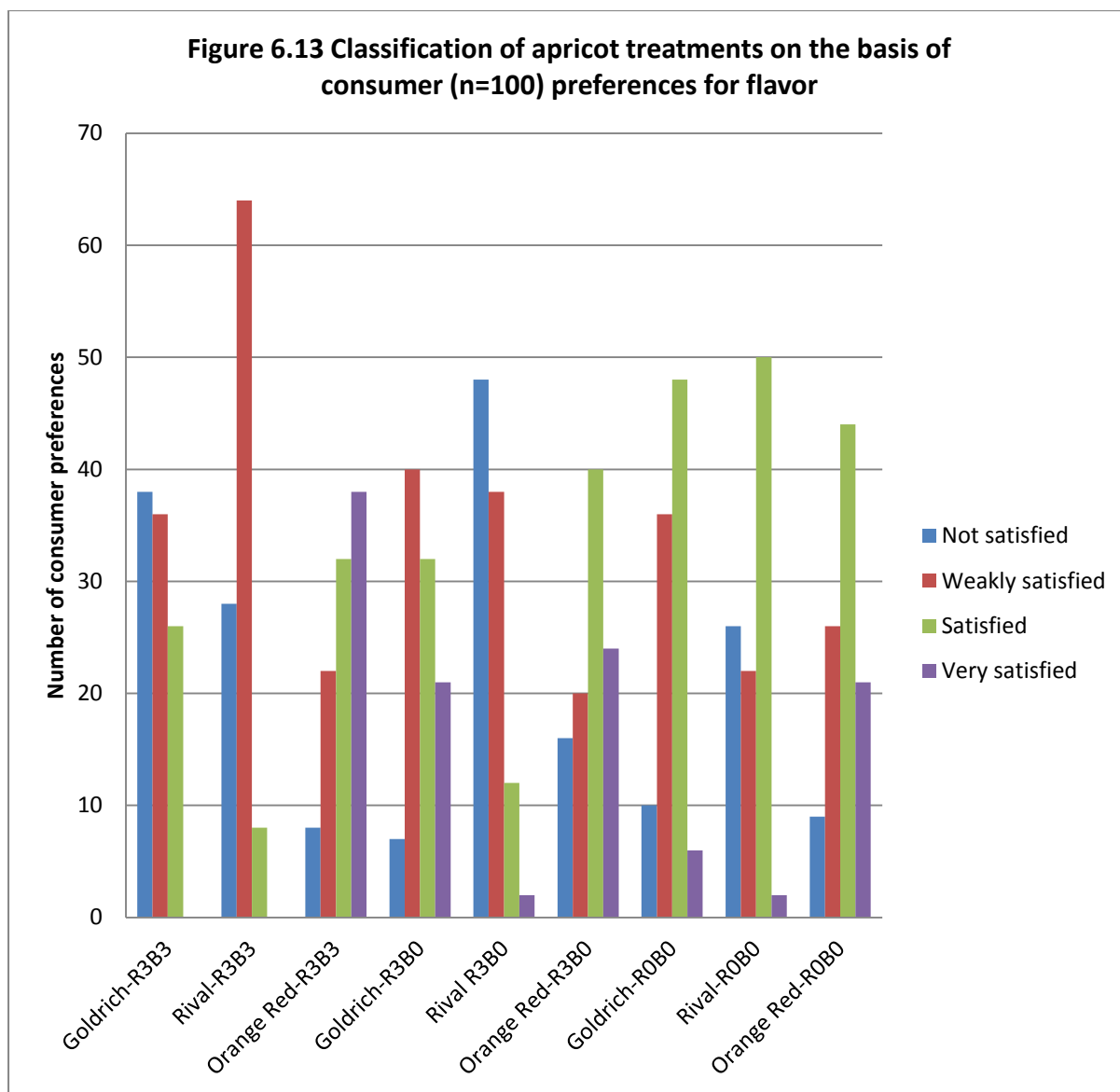
Based on the weighted average scores were; Goldrich=-0.26; Rival=-0.55; Orangered® Bhart = -0.11; R3B3=-0.42; R3B0=-0.29; and R0B0=-0.20 which suggests that the maximum ReTain® and boron treatments additively decreased the ripeness of the apricots. This supports the previous results where the R3B3 treatment increased the firmness and decreased the sweetness of apricots.

Orangered® Bhart was the most preferred variety in terms of ripeness by 61% of consumers who considered it ripe. This was followed by Goldrich and Rival. 40% of consumers perceived Rival as unripe and 38% consumers rated Goldrich as midripe. ~49% of consumers rated R0B0 treated apricots to be ripe and most of the consumers rated R3B3 and R3B0 treated apricots as midripe or unripe apricots. The  $\chi^2$  analysis showed that there were significant differences in perceived ripeness among the 3 varieties (Table 6.4). More importantly  $\chi^2$  analysis showed that there were significant differences in perceived ripeness among the 3 treatments across varieties as shown in Table 6.5.

#### **6.4.7 Consumer perception of apricot samples for flavor**

Consumers rated each sample on a 4 point scale (not satisfied, weakly satisfied, satisfied and very satisfied) where they were instructed to rate each sample relative to their individual notion of ideal sweetness of apricots. The results were analyzed by coding them as -1 for not satisfied at all, -0.5 for weakly satisfied, 0 for satisfied and 1 for very satisfied.

Based on the weighted average scores were; Goldrich=-0.26; Rival=-0.55; Orangered® Bhart= -0.11; R3B3=-0.42; R3B0=-0.29; and R0B0=-0.20 which suggests that maximum ReTain® and boron treatment decreased the flavor of the apricots. This is supported by the results presented above where the R3B3 treatment increased the firmness and decreases the sweetness and perceived ripeness of apricots.



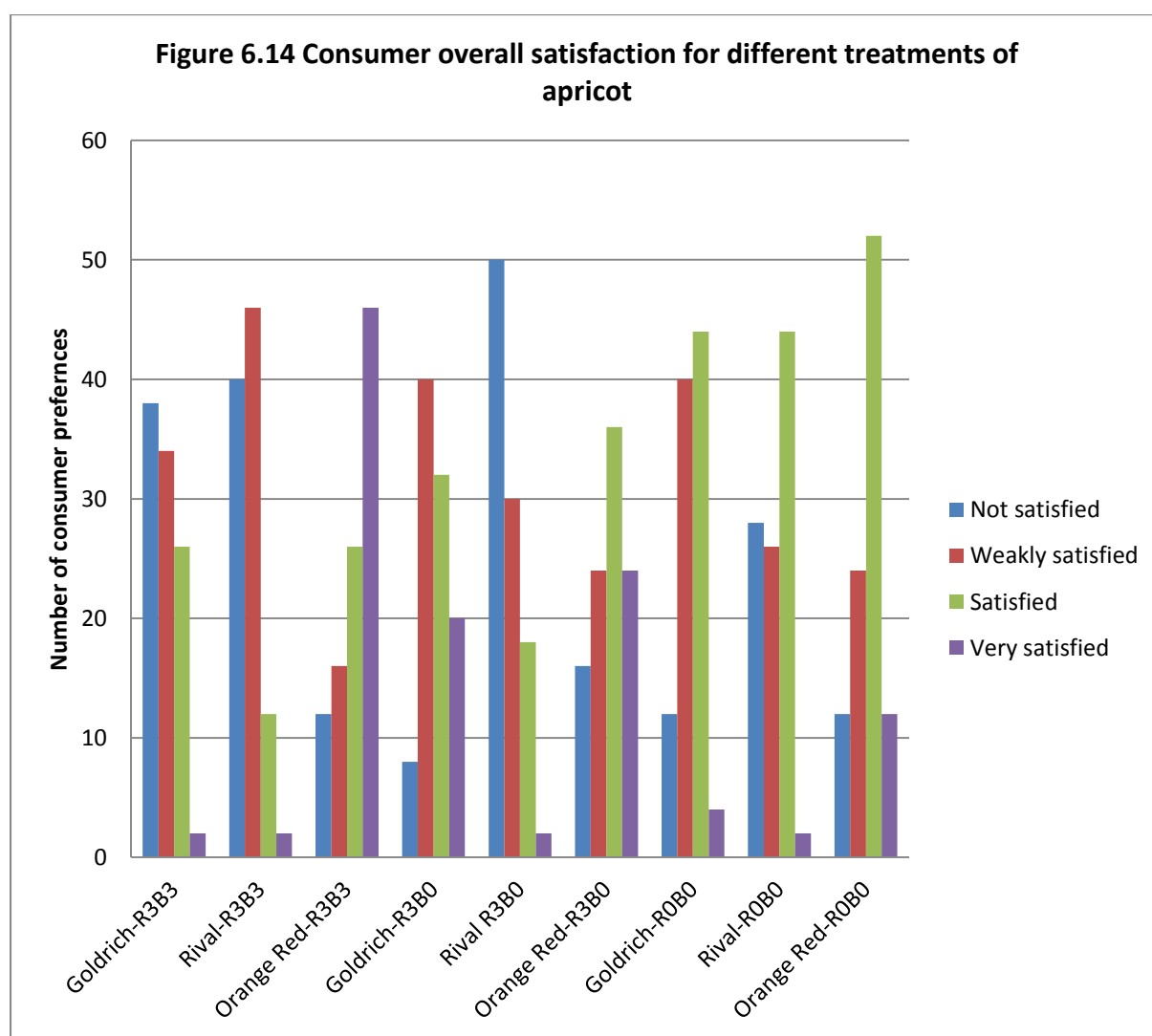
A  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived flavor among the 3 varieties ( $\chi^2$  is equal to 39, 134 and 45 for G: R, R: OR and OR: G respectively). More importantly  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived flavor among two of the treatment comparisons ( $\chi^2$  is equal to 26 and 43 for R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5. This suggested ReTain® in particular decreased the flavor of apricots.

Orangered® Bhart was the most preferred variety in terms of flavor with 66% consumers rating them as satisfactory or better followed by Goldrich (44%) and Rival at 25%. 37% of consumers were not satisfied with Rival. ~56% of consumers rated R0B0 treated apricots to be of acceptable flavor or better. Most of the consumers rated R3B3 and R3B0 treated apricots as unsatisfying for flavor which suggests that maximum amount of ReTain® can affect the flavor of fruits.

### 6.4.8 Consumer perception of apricot samples for overall satisfaction

Consumers rated overall satisfaction of apricots on a 4 point scale (not satisfied, weakly satisfied, satisfied and very satisfied) where they were instructed to rate each sample relative to their individual notion of overall satisfaction of different quality attributes of samples. The results were analyzed by coding them as -1 for not satisfied at all, -0.5 for weakly satisfied, 0 for satisfied and 1 for very satisfied. 38% of consumers were satisfied with Orangered® Bhart while 34% of consumers were over all satisfied with Goldrich variety. 22% of consumers were very satisfied with R3B3 treatments followed by 15% consumers for R3B0 treatments.

A  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived overall satisfaction for 3 varieties ( $\chi^2$  is equal to 38, 121 and 47 for G: R, R: OR & OR: G respectively). More importantly  $\chi^2$  analysis showed that there were significant differences ( $p < 0.0001$ ) in perceived satisfaction for two treatments across varieties ( $\chi^2$  is equal to 29 and 53 for R3B0:R0B0 and R3B3:R0B0 respectively) as shown in Table 6.5.



**Table 6.6 Individual means for consumer (n=100) determined quality scores characteristics obtained for nine different treatments**  
**(Three varieties by three ReTain®/boron levels)**

Quality parameters	Size	Color	Sugar	Acidity	Firmness	Ripeness	Flavor	Overall Satisfaction
Score number	5	3	4	4	3	4	4	4
Score values	-1 = Too small -0.5 = small 0 = Average 0.5 = big 1 = Too big	-1 = not colored 0 = Average 1 = Too colored	-1 = not sweet -0.5 = not enough sweet 0 = Average 1 = Too sweet	-1 = not acidic -0.5 = not enough acidic 0 = Average 1 = Too acidic	-1 = not firm 0 = Average 1 = Too firm	-1 = Unripe -0.5 = not enough ripe 0 = Average 1 = Too ripe	-1 = not satisfied -0.5 = not enough satisfied 0 = satisfied 1 = very satisfied	-1 = not satisfied -0.5 = not enough satisfied 0 = satisfied 1 = very satisfied
Treatment	Mean Scores							
<b>ORR3B3</b>	-0.43 <sup>g</sup>	0.40 <sup>b</sup>	<b>-0.02<sup>a</sup></b>	<b>-0.05<sup>d</sup></b>	<b>0.11<sup>c</sup></b>	<b>-0.11<sup>ba</sup></b>	<b>0.26<sup>a</sup></b>	<b>0.30<sup>a</sup></b>
<b>GR3B3</b>	0.40 <sup>c</sup>	-0.38 <sup>f</sup>	-0.47 <sup>ed</sup>	0.53 <sup>a</sup>	0.53 <sup>a</sup>	-0.53 <sup>d</sup>	-0.54 <sup>d</sup>	-0.48 <sup>de</sup>
<b>RR3B3</b>	<b>0.15<sup>ed</sup></b>	<b>0.00<sup>c</sup></b>	-0.46 <sup>ed</sup>	0.32 <sup>b</sup>	0.67 <sup>a</sup>	-0.64 <sup>d</sup>	-0.60 <sup>d</sup>	-0.61 <sup>c</sup>
<b>ORR3B0</b>	<b>0.06<sup>ef</sup></b>	0.71 <sup>a</sup>	<b>-0.16<sup>bc</sup></b>	<b>-0.09<sup>d</sup></b>	0.28 <sup>b</sup>	-0.17 <sup>b</sup>	<b>-0.04<sup>b</sup></b>	<b>-0.01<sup>b</sup></b>
<b>GR3B0</b>	0.79 <sup>a</sup>	-0.30 <sup>fc</sup>	-0.24 <sup>c</sup>	0.14 <sup>c</sup>	<b>0.12<sup>c</sup></b>	<b>-0.09<sup>ba</sup></b>	-0.08 <sup>b</sup>	<b>-0.07<sup>b</sup></b>
<b>RR3B0</b>	0.20 <sup>d</sup>	<b>-0.12<sup>de</sup></b>	-0.53 <sup>e</sup>	0.49 <sup>a</sup>	0.58 <sup>a</sup>	-0.58 <sup>d</sup>	-0.62 <sup>d</sup>	-0.60 <sup>c</sup>
<b>ORR0B0</b>	<b>0.015<sup>f</sup></b>	<b>-0.14<sup>d</sup></b>	<b>-0.09<sup>ba</sup></b>	<b>0.00<sup>d</sup></b>	<b>-0.04<sup>d</sup></b>	<b>-0.05<sup>a</sup></b>	<b>0.03<sup>b</sup></b>	-0.08 <sup>b</sup>
<b>GR0B0</b>	0.55 <sup>b</sup>	-0.17 <sup>de</sup>	-0.23 <sup>c</sup>	0.29 <sup>b</sup>	0.18 <sup>cb</sup>	-0.15 <sup>ba</sup>	-0.23 <sup>c</sup>	-0.29 <sup>c</sup>
<b>RR0B0</b>	0.25 <sup>d</sup>	-0.18 <sup>de</sup>	-0.39 <sup>d</sup>	0.25 <sup>cb</sup>	0.20 <sup>cb</sup>	-0.38 <sup>c</sup>	-0.31 <sup>c</sup>	-0.38 <sup>de</sup>

<sup>1</sup>Treatments as listed in Table 6.1. 2

Means with same letters are not significantly different at P< 0.001 using LSD in GLM model.

Bold numbers are the most preferred value for quality parameters of apricots.

#### 6.4.9 Summary of the consumer derived scores for all individual treatments

Table 6.6 lists the interaction table for the values of the derived scores for all individual treatments across boron/ ReTain® and varieties giving their levels of significance. As shown in Table 6.6, untreated Orangered® Bhart was the most preferred treatment being in the top 3 scores for 7 of 8 categories though just out of the top for overall satisfaction. Indeed Orangered® Bhart was overall the most preferred variety being in the top 3 for 18 of 24 possible occasions. In contrast both Goldrich and Rival only managed 3 occasions each.

The results for the boron/ ReTain® treatments were not as clear cut with R0B0, R3B0 and R3B3 having 7, 9 and 8 scores in the top 3 respectively. Thus the boron/ ReTain® treatments may need careful management to ensure optimal consumer preferences are maintained.

### 6.5 Results and Discussion: Consumer preferences compared with instrumental data

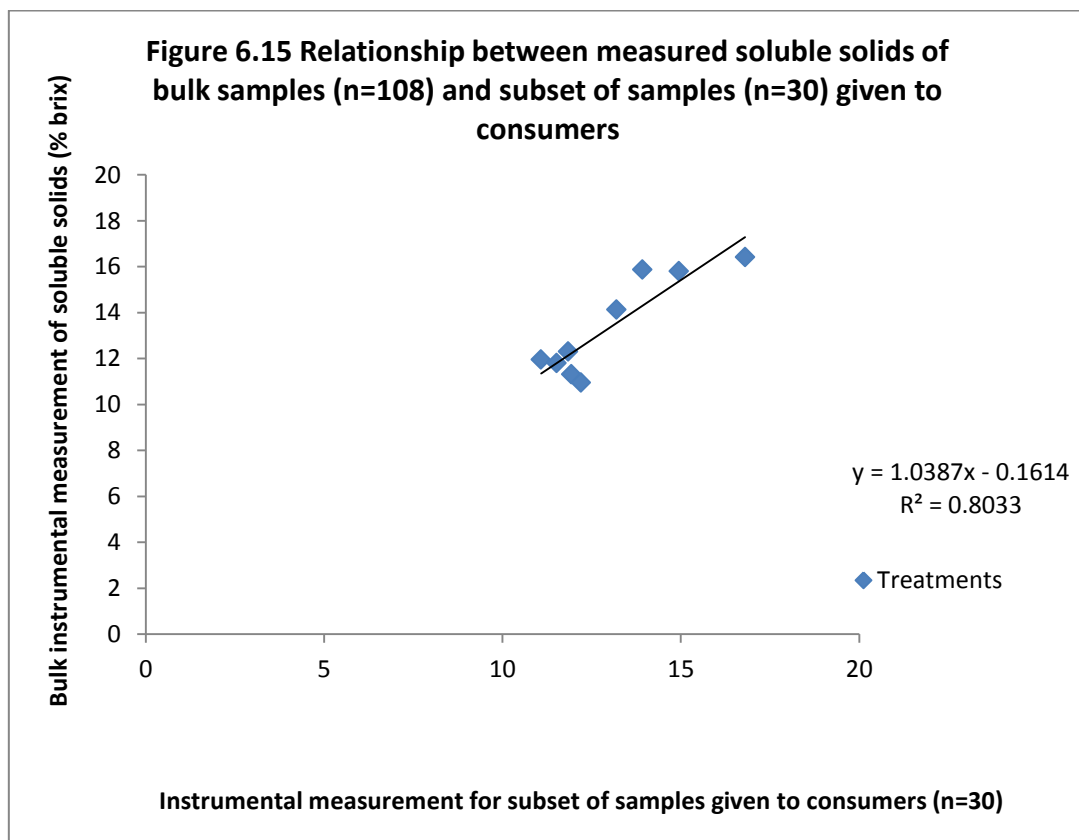
The search for correlations between sensory and instrumental measurements was conducted for several reasons: 1) the need for quality control instruments; 2) the desire to predict consumer response; 3) the desire to understand what is being perceived in sensory assessments; 4) the need to develop improved/optimized instrumental test methods; and finally, 5) to construct testing equipment that will duplicate/replace sensory evaluation.

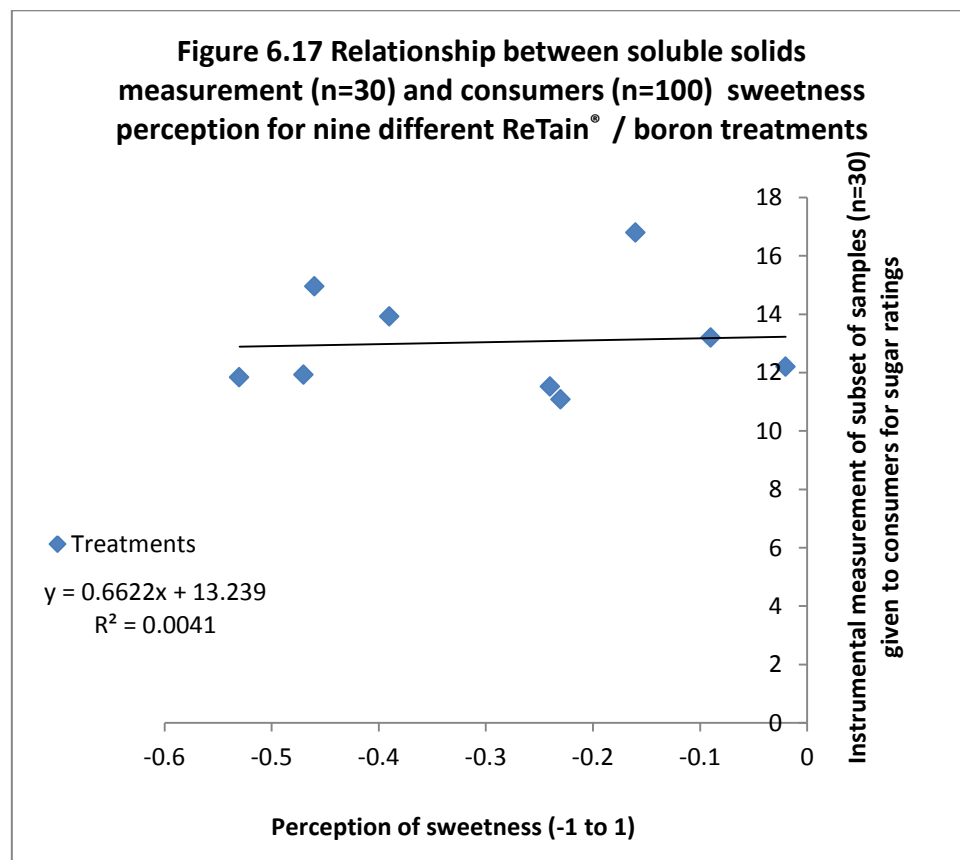
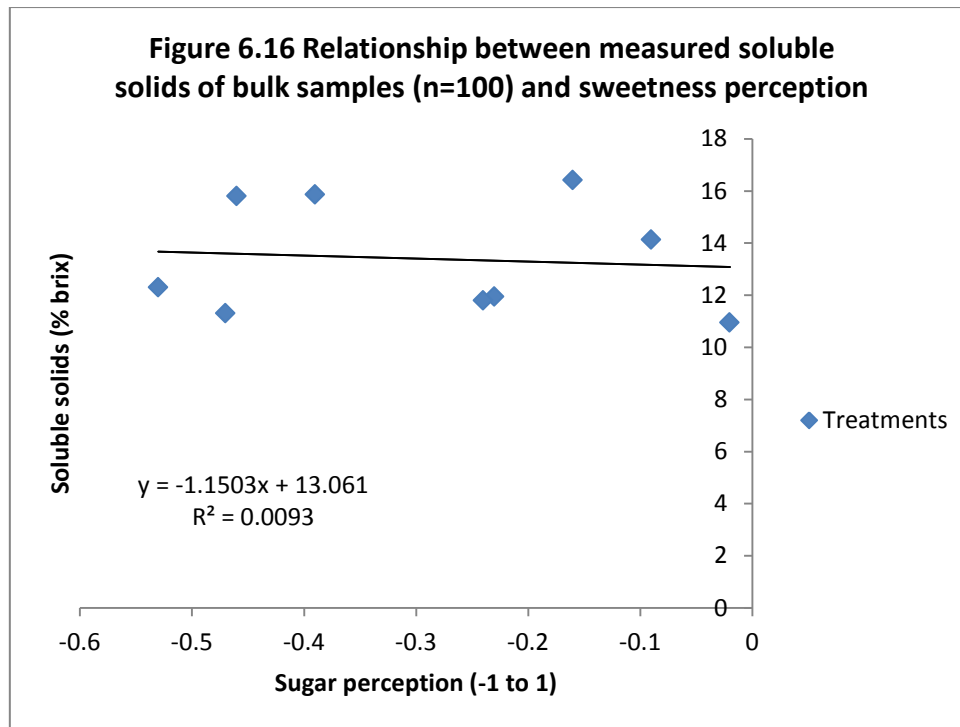
The application of sensory analysis using a panel of selected and trained tasters was a reliable and effective method for the evaluation of the organoleptic quality of boron and ReTain® treated apricots. These data will give better understanding of the acceptability of 'in orchard' treatments for commercial orchardist and growers. The expectation of the survey was to derive good correspondence between the laboratory analyzed attributes and the sensory attributes for characteristics such as sweetness and firmness. Others such as taste, color and ripeness were not expected to be so easily measured by laboratory analysis and were not expected to agree as well with sensory panels (Lespinasse *et al.*, 2006). Sensory analysis thus remains an indispensable tool both in its own right and to ground truth laboratory analyses.

Figure 6.15-17 shows the soluble solids relationships between bulk apricot samples, a subset of this bulk samples (BS) used in the actual consumer tests and consumer perception for nine different treatments. The full regression analysis details for all parameters are given in Table 6.7. The samples were instrumentally analyzed with methods described in Chapter 3. The laboratory analysis was a part of Chapter 4, where 16 different treatments were analyzed for boron and ReTain® effects. These samples used high numbers

of fruits per treatment (n=12) for each treatment and were addressed as bulk samples. However, a smaller number of fruits used in the taste test (n=30) were analyzed with the same method from the subset of samples used in tastings. At least three samples from each treatment used in the survey were analyzed instrumentally. This forms the subset of the bulk samples and is listed as subset samples (SS). Finally the scores for consumer perception presented above were used (Table 6.4 and Table 6.5).

As shown in Figure 6.15 there was a significant relationship between the results obtained by BS and SS for total soluble solids ( $r^2 = 0.80$ ) at a 95% confidence level. However, there was a non-significant weak relationship between consumer perception and BS ( $r^2 = 0.009$ ). The results were non-significant with SS and consumer perception ( $r^2 = 0.004$ ). Figure 6.17 shows that the overall relationships between bulk samples and perceived score data was poor. When the subset of samples (SS) was compared to the perceived score data it was no better and still not significant and it gave an intercept of 13.2. Therefore instrumental analysis is not the perfect way to know consumer attitudes, but they give some relevant information about the desired level and association direction of the quality parameter. In the same manner firmness, acidity and size were compared in Table 6.7.





**Table 6.7 Slope from regression equation and coefficient of determination ( $r^2$ ) comparing instrumental analysis (n=30), Bulk instrumental analysis (n=108) and consumer analysis (n=100) for the 9 treatments tested.**

	Instrumental data (SS) vs. Bulk Instrumental data (BS)		Perceived data vs. Bulk Instrumental data (BS)		Instrumental data (SS) vs. Perceived data				
	R <sup>2</sup>	P value	R <sup>2</sup>	P value	Intercept	P-value	Slope	R <sup>2</sup>	P-value
<b>Size</b>	0.536	0.025*	0.257	0.16	112.44	0.00*	-0.0031	0.017	0.74
<b>Sugar</b>	0.803	0.001*	0.009	0.81	13.23	0.00*	0.0060	0.004	0.87
<b>Acidity</b>	0.885	0.00*	0.112	0.38	12.805	0.00*	0.0421	0.279	0.14
<b>Firmness</b>	0.758	0.002*	0.002	0.89	30.61	0.00*	0.0211	0.083	0.45
* indicates significant at $p \leq 0.05$									

It can be seen that the bulk and subset samples were strongly related as expected. Thus the material supplied to consumers was a good representation of the bulk sample (Table 6.7 column 1). Better  $R^2$  values were obtained for the SS instrumental data and perceived scores for acidity and firmness. Correlations were also carried out among the quality attribute values. There was a negative correlation between fruit size, acidity, firmness and sugar. The samples used for the tastings and those analyzed in the laboratory were probably slightly different in terms of quality parameters thus it was the regressions of SS and perceived data that were the most telling. The relationship between sugars and perceived sweetness was the least significant. The consumers were then least consistent with measured values for the size of the fruit, but were somewhat consistent for acidity ( $p=0.143$ ,  $r^2=0.28$ ).

There was a no significant ( $p=0.451$ ) relationship between firmness ratings and measured firmness ( $r^2=0.082$ ). The reproducibility of the measurements of samples was significant for bulk samples and samples offered to consumers. Low acidity and firmness were judged to be important quality descriptors for apricots that potentially may be associated well with instrumental analyses. It is important to understand that the fruit presented to the consumers were not substantially different in most of these characteristics. Thus the cues for perception could be influenced by other factors. For example among sensory attributes sweetness was often associated with pleasant aroma, and ripeness as well sugar or soluble solids content. The difficulty in identifying major effects of the treatments might be due to the fact that every single person is not necessarily



influenced by the same sensory attributes and the quality scale and what creates and confounds it (e.g. for sweetness: sugars, acidity, firmness, volatiles) may vary strongly from one person to another.

Color was very important to consumers for assessing the quality and maturity of fruit. The Orangered® Bhart variety, which was rated superior for its sweetness had a red blush on the side of the fruits and consumers, found it too colored. These results were similar to pear studies where a dark red blush on pear was disliked by consumers (Kappel *et al.*, 1995). The size of the red blush on the Orangered® Bhart variety made it difficult for consumer acceptance. The color is a good indicator of ripeness at harvest, however, as the survey results indicated the red patched Orangered® Bhart fruit cannot be considered as having an indicator of high taste quality or a sign of ripeness.

## **6.6 Conclusions**

Orangered® Bhart was the most preferred variety by consumers followed by Goldrich and Rival. This is distinct from the results discussed in Chapter 5 for flavor, where volatiles of individual treatments analyzed with HS SPME suggested that Rival would be the best variety. However, consumers rated Orangered® Bhart with R3B3 treatment the most preferred variety. The maximum amounts of boron and ReTain® have certainly improved the flavor of the Orange red variety.

The R3B3 treatment gave firmest fruits for all three varieties. Consumers found Orangered® Bhart variety to have enough sweetness with the R3B3 treatment; however, Goldrich and Rival were too acidic and lacked enough flavor. R3B0 produced sweet and ripe fruit for Goldrich and Rival. This suggests that the effect of the highest amount of ReTain® (1 kg/ha) is variety specific, though it is certain that consumers perceived this treatment to be successful compared to the other eight boron and ReTain® treatments.

Rival and Goldrich samples was firm due to the effects of the R3B3 treatments. The firm fruits exhibit increased acidity of the fruits, which was not enough to detect in Orangered® Bhart but was easily detected by consumers in Rival and Goldrich. The optimum fruit through instrumental analysis was sometimes found not to be consistent with values given by consumers and trained panelists across a range of quality parameters.

The overall appreciation by the consumers correlated well with the variety of the apricots but for most of the attributes no significant correlation was found. The heterogeneity of the fruit samples was thought to be responsible for the non-exact regressions of BS and SS. Moreover, consumers find difficult to differentiate range of sourness (acidity) in between the samples.

Fruit firmness presented interesting results where maximum boron and ReTain® treatment gave excellent firmness to the Orangered® Bhart and Rival varieties. The optimum firmness should be equal to the rating of 0, which was 42-55 N. Using the optimum rating 0 for sweetness, optimum SSC ranged from 11-14 % for the tested samples. The relationship between SSC and TA were treatment dependent. It was difficult for panelists to understand the sweet/sour balance.

The survey had a common analysis between trained panelist and consumer evaluations. Consistent differences were noted between the two groups which made the work of panels very attractive, as they are less variable in opinion and may be used in lesser numbers compared to consumers. The report of Shepherd *et al.* (1988) states to avoid the use of trained panelists to provide measures of preference or acceptance. This approach will adequately work with buying behavior of the consumers but cannot be implemented in the present studies. The trained panelist was essential to justify the sensory analysis of apricot as consumers lacked the ability to judge the quality parameters with different treatments on the same variety.

The consumer tests could be differently organized in terms of its composition. Setting up homogeneous consumer groups in terms of age, sex, income, etc. would certainly give interesting and probably more consistent results though would not give a measure of general community response.

To sum up, the ideal apricot appears to have the following characteristics by comparison of consumer and instrumental data: fruit diameter in the range of 60 mm -70 mm (120 to 150 g); a dark orange skin, firmness of 28-35 N, SSC of 13 -15 % with TA~ 14-18 mg malic acid per 100 ml juice. However, poor agreement between instrumental and consumer perceptions means that such surveys needs to incorporate participation and open-ended questions to some degree, which will allow for the depth of discussion, exploration, and self-analysis.

A regular, intensive and long training session could help to improve surveys of this sort; however, it is a time consuming and cost intensive step. In order to enhance the accuracy and the reliability of the assessment of the appropriate apricot treatments that consumers can differentiate further work will be required.

## CHAPTER 7

### CONCLUSION

#### 7.1 Program goals

The overall goal of this study was to aid in producing better quality apricot fruit by developing a greater understanding of the factors that affect quality and the characteristics that contribute to quality. Of particular importance was understanding whether the firmness of the fruits could be improved by foliar application of boron and ReTain® and how that interacted with the different ways to ascertain quality (physical and crude chemical, volatiles and hedonistic). To achieve this overall goal the work was divided into four main objectives

**Objective 1:** To develop a suite of technological capabilities for conducting apricot quality measurements. The measurements will be of characters that affect consumer perceptions of apricot quality.

**Objective 2:** To characterize interactions among the treatments of Boron and ReTain® across three varieties ('Rival', 'Goldrich' and 'Orangered® Bhart') representative of major Tasmanian cultivars. These interactions will be characterised via post harvest measures in the a) physico chemical properties and b) volatiles measures, due to the treatments. To compare the levels of sugars, organic acids, volatiles, B mineral content and analyse the changes in the quality attributes to gain a better understanding of development of quality for apricot fruits.

**Objective 3:** To determine effects of boron inputs on apricot fruit and physiological status during apricot growth and development in order to give strength to the outer skin of the apricot and thereby improve the firmness and fruit retention of apricot.

**Objective 4:** To measure consumer satisfaction with retailed apricot quality and link this back to outputs from objectives 2 and 3.

The research relating to these objectives was presented in four experimental chapters (Chapter 3: method development; Chapter 4: instrumental quality assessment; Chapter 5: volatiles composition and Chapter 6: Hedonistic assessment) as shown in the model of the entire work on page 10. Each component in this model (developing a set of quality parameter tests, spraying apricots with boron and ReTain®, analyzing samples for treatment effects on quality, volatiles characterization of 16 different treatments and 3 varieties of apricots, consumer preferences for treated samples) is related to all the other components to create a holistic, integrated model of quality development in apricot.

The results analysed from each component in this research will provide a sound scientifically derived information base to generate improvement in the quality parameters of Tasmanian apricots.

## **7.2 Assessment against objectives**

Fresh apricots tend to possess a very short shelf life of six to seven days and transport of the fruit within this limited timeframe from farm to market is a major concern due to the soft skin of the fruit. Foliar applications (eg of boron and ReTain®) might improve the overall quality parameters of apricot especially the firmness attribute that will delay the ripening of fruit. Increases in possible post harvest storage time will allow Tasmanian growers to export apricot to more countries and increase their export income.

### **7.2.1 Objective 1**

Objective 1 was achieved by developing a set of technologies in the available laboratory setup to analyse different quality attributes of apricots. These included measures of tree /fruit mineral composition, fruit sets, fruit drops and flower bud loads. They also included fruit physical (size, color and firmness) measures, fruit crude chemical (sugars, pH and acids) and fruit volatiles. Reproducibility of the measures were good through out the experiments. The different methods used and their relationship with the available literature are discussed in Chapter 3. Overall it was thus possible to use these measures to understand the possible causes of consumer perceptions and to understand the influences of treatments on apricot quality as required by the later objectives.

### **7.2.2 Objective 2 .1 Physico Chemical properties**

The field trial covered a representative range of cultivars, rootstock and tree ages for two growing seasons in different environmental conditions and uniform cultural conditions (e.g. soil type, fertilization, drainage). The trials were conducted on three different varieties namely Rival, Goldrich and Orangered® Bhart for two seasons (Year 2009-2010). The boron sprays were repeated four times and ReTain® sprays were repeated twice to study cumulative effects of ReTain® (plant growth regulator) and boron treatments on the same trees over two years. The results given in Chapter 4 revealed that both boron and ReTain® sprays could improve the firmness attributes of Rival, Goldrich and Orangered® Bhart apricots. In particular ReTain® sprays were highly consistent and beneficial in this regard.

The combined effect of boron and ReTain® improved the total fruit set along with firm fruit without substantially adversely affecting other fruit qualities. The effects of ReTain® were variety specific and did slightly reduce the sugars level of Goldrich in the present studies.

In summary the foliar application of boron and ReTain® improved the overall quality parameters of apricot especially the firmness attribute. This can delay the ripening of fruit and Increase the period after harvest time when fruit are acceptable to consumers. Consequently this will allow Tasmanian growers to export apricot to more countries and increase their export income.

### **7.2.3 Objective 2 .2) Changes in Volatiles profiles**

The detailed analysis of changes in the aromatic profile of individual varieties due to treatment effects of boron and ReTain® provides a useful indication of overall fruit quality and solving the issues of Objective 2b as well as allowing greater understanding of possible reasons why consumer and instrumental physico-chemical assessments may not agree. For example chemically determined 'sweetness' (Brix) may disagree with consumer determined 'sweetness' due to interactions with esters and other volatiles perceived as 'sweet', 'sour' etc. So In addition to measuring physical and chemical parameters, we used the HS SPME technique followed by GC MS to define aroma components and get a more complete evaluation of the effects of the treatments used.

The adsorbed flavor components were analyzed for all 16 treatments of boron and ReTain® for three cultivars that resulted in extraction of 30 volatiles. The three cultivars had different behaviors for the extraction of volatiles due to the treatment effects. As indicated in Chapter 5, Table 5.1 though the total amount of volatiles eluted in Rival were maximum, the spray program had least effect on it compared to Goldrich and Orangered® Bhart.

Individual volatile components (VC) were not sufficient to differentiate among all three varieties across the different treatments. The differences in the concentration of individual groups of VC were a better determinant of the varieties and treatment effects. The concentrations of volatile compounds that were glycosidically bound depended on apricot variety and the extraction technique used. The application of boron had significantly increased the terpenes and terpene alcohols of Goldrich, although the effects of ReTain® were prominent on VC of Goldrich and Orangered® Bhart as mentioned in Table 5.10 (Chapter 5).

The final conclusions were thus that no simple overall effect on volatiles existed and there would be a need to assess flavor profile for each treatment applied to an orchard. However, the later consumer tests indicated that big changes in volatiles composition were acceptable to consumers suggesting that treatments may make reasonable changes to VC without great effects on market acceptability.

### 7.2.4 Objective 3

The results of ICP-OES analysis gave evidence of increased absorption of boron into leaves, branches and fruits at different stages of fruit development with increasing levels of B sprays. Effects on other minerals were minor. As observed in Chapter 4 this increased absorption of B slightly, but significantly. As all treatment levels of B exceeded 20 ppm it would seem levels greater than this are still inhibitory to some physiological processes in apricots. The preharvest foliar application of boron increased the flowerbuds and fruit set for all three varieties. The numbers of fruit dropped was also reduced. The results were consistent for both the seasons. The quality parameters of apricots at harvest were also affected by the sprays in all three varieties. Thus greater understanding of developmental effects of B were attained which can be used to link to pruning and thinning programs for optimal apricot production.

### 7.2.5 Objective 4

Since consumer perception is ultimately the most important assessment in fruit quality, we submitted the selected treatments of three cultivars for quality evaluation. Unexpectedly, the consumers were unable to discriminate between the treatments based on the quality previously measured attributes. There was particularly weak relationships between the instrumental analysis and consumer preferences.

Orangered® Bhart scored the highest overall acceptability for flavor attributes and consumers were partly able to identify the increases in the firmness of R3 treatments of ReTain®. The HS-SPME GC MS technique detected significant and large differences between the VC profiles of varieties and treated apricots. However, the differences that were able to be detected instrumentally were either imperceptible to human sensation or were counteracted by other differences. This result requires further studies regarding the nature of those volatile compounds that affect overall apricot flavor as identified by Guillot *et al.* (2006).

## 7.3 Conclusions

In this study a great number of data, including physicochemical properties and volatile constituents of Rival, Goldrich and Orangered® Bhart cultivars were obtained with different treatments of B and ReTain®. The results showed that the most significant and larger changes i.e. increase in the firmness, color, increase in terpenes, terpene alcohols and esters of the cultivars mainly took place due to the effects of ReTain®. Boron had significant increased flowerbud numbers and fruit set along with the increase in VC in Goldrich. We can recommend from these data the use of B and ReTain® spray programs in apricot orchards for managing quality under appropriate circumstances. However, the stage of the

tree at foliar spray application, the desired fruit load, existing B level and concentration of the sprays are also critically important. ReTain® is recommended only for certain cultivars of apricots such as Rival and Goldrich. A trial on a small number of trees before extending to whole orchard would be recommended for better results.

In addition the better defining cultivars in terms of fruit quality characteristics which may provide information on suitability to particular markets, our observations provide useful information for choosing best combinations of concentrations (R2B3 for volatiles and R3B2 for firmness) to receive maximum benefits from the foliar spray program. Data obtained in this study are the first data produced for the effects of these sprays on three cultivars of Tasmanian apricot. The spray programs information is currently provided to the farm manager of Qew orchards in Tasmania and they have incorporated B and ReTain® as a part of their annual management program.

## **7.4 Future research recommendation**

Most changes in the volatile metabolites, including those unrelated to fruit aroma, occur during ripening. Ethylene is one such unscented VC that is heavily involved in modulating the volatile emission of apricots (Botondi *et al.*, 2003). It would be interesting to experiment with the combined effects of boron and ReTain® directly on ethylene production and responses and observe the changes associated with it. This could assist in the understanding the causes of how the changes in physico-chemical, volatiles and consumer perceptions arose.

Studies of Botondi *et al.*, have revealed that 1-MCP inhibits ethylene production in apricots and can help to maintain firmness like ReTain® but modifies the aroma profile. However, with the appropriate amount of usage of ReTain® the aroma is not critically affected in our present studies. The research could proceed further with more cultivars with 1-MCP and ReTain® to analyse the changes associated with their application in quality attributes to determine whether their physiological effects were via similar pathways.

A detailed analysis of aromatic profile for different B and ReTain® treatments may represent an efficient tool for classification of a broad range of genotypes by important quality attributes. Volatiles with relevant odor contributions may serve as quality markers for selecting towards an extended ripening season or consumer preferred flavor. Measuring the levels of certain VC with relevant odor contributions (i.e linalool, cymene,  $\alpha$ -terpeneol) that were found in the present study could possibly assist in identifying the optimal harvest time of apricots.

As is evident, detailed information about color attributes was not instrumentally analysed in the present study. This was even though statistically significant changes were found for some treatments (Table 4.5). While anthocyanins have received most attention in fruits of other *Prunus* species, including peach, nectarine and sweet cherry, studies on anthocyanins in apricots are rare. A study for the effects of boron and ReTain® foliar application on pattern of anthocyanins and  $\beta$ -carotene could be researched due to the importance of visual clues in consumer perception.

Overall different cultivars of the apricots could be objectively screened using standard extraction procedures to identify physicochemical and aromatic profiles to enhance our efficiency in attaining breeding objectives.

Ultimately future research will need to follow up measures of quality and the physiological causes of changes resulting from in orchard treatment effects as we continue to try and better meet consumer expectations and provide better consumer experiences consequently continuing returns to apricot growers.



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## Appendix 1. Fresh production of apricots by country in MT

(Year of Estimate: 2008)

Rank	Country	Production (MT)	
1	China	1,725,000.00	
2	Turkey	540,000.00	
3	Italy	218,000.00	
4	France	170,500.00	
5	South Africa	100,000.00	
6	Spain	90,000.00	
7	United States	78,930.00	
8	Greece	74,400.00	
9	Russian Federation	37,000.00	
10	Chile	26,600.00	
11	Austria	24,000.00	
12	Poland	2,400.00	
13	Germany	500.00	
14	Algeria	0.00	
15	EU-27	0.00	

**Source:** United States Department of Agriculture

## Appendix 2. List of countries by apricot production in 2008.

Rank	Country/Region	Apricot production (tonnes)	Rank	Country/Region	Apricot production (tonnes)
>100,000 tonnes			50,000-100,000 tonne		
1	 Turkey	716,415	12	 France	94,526
2	 Iran	487,333	13	 Ukraine	88,900
3	 Pakistan	325,779	14	 China	77,812
4	 Uzbekistan	265,000	15	 Greece	77,400
5	 Italy	205,493	16	 United States	74,040
6	 Algeria	172,409	17	 Hungary	68,155
7	 Japan	120,600			
8	 Morocco	113,216			
9	 Egypt	106,165			
10	 Spain	103,400			
11	 Syria	100,900			
10,000-50,000 tonnes					
18	 Russia	49,000			
19	 South Africa	43,593			
20	 Romania	32,125			
21	 Lebanon	32,000			
22	 Turkmenistan	32,000			
23	 Tunisia	26,500			
24	 Tajikistan	26,000			
25	 Argentina	25,500			
26	 Afghanistan	25,000			
27	 Armenia	24,000			
28	 Serbia	22,301			
29	 Azerbaijan	21,494			
30	 Iraq	18,952			
31	 Chile	18,000			
32	 Australia	17,327			
33	 Libya	17,000			
34	 Kyrgyzstan	16,600			



35	 Austria	15,327
36	 Bulgaria	12,957
37	 Israel	10,002
38	 India	10,000

Source: Food and Agricultural Organization of the United Nations accessed in April 2011.  
The total world apricot production for 2008 was 3,758,936 tonnes.

### APPENDIX 3: SAMPLE OF QUESTIONNAIRE

#### PART 1: BACKGROUND INFORMATION

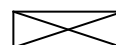
PLEASE ANSWER THE FOLLOWING QUESTIONS BY CROSSING (X) THE RELEVANT BLOCK OR WRITING DOWN YOUR ANSWER IN THE SPACE PROVIDED

EXAMPLE of how to complete this section of questionnaire

Your Gender

MALE

FEMALE



This section of the questionnaire refers to background or biographic information. Although we are aware of the sensitivity of the questions in this section, the information will allow us to compare groups of respondents. Once again we assure you that your response will remain anonymous. Your co-operation is appreciated.

1. Gender

Male	
Female	

2. Age group

Less than 18 years	
18 - 30 years	
31 - 45 years	
46 - 60 years	
61 - 75 years	
Above 75 years	

3. How would you describe your economic status?

Poor	
Below average	
Average	
Above average	
Affluent	

4. Your highest educational qualification

Primary School education/ High School education	
Diplomas	
Bachelor Degree(s)	
Master Degree(s)	
Ph.D	

5. How would you describe the area in which you reside?

Urban	
Rural	

6. How many times do you go shopping for fresh fruit per week?

Everyday	
Four times a week	
Twice or three times a week	
Once a week	
Never eat fruit	
Grow fruit at home	

7. Do you eat apricots?

Yes	
No	

## PART 2: CONSUMER PREFERENCES FOR QUALITY OF APRICOTS

This section of the questionnaire explores the preferences of quality attributes of apricots desired by consumers.

1. What form of apricots do you prefer most?

Fresh apricots	
Stored apricots	
Sundried apricots	
Canned apricots	
Apricot jam, jelly etc.	

2. What is the most important characteristics required in an Apricot?

Flavour	
Aroma	
Colour	
Firmness	
Size	
Shape	
Any other to mention	

3. In what criteria would you judge the fruit size of following samples?

	TOO SMALL	SMALL	AVERAGE	BIG	TOO BIG
SAMPLE A					
SAMPLE B					
SAMPLE C					
SAMPLE D					
SAMPLE E					
SAMPLE F					
SAMPLE G					
SAMPLE H					
SAMPLE I					

4. How do you find the outer skin colour of following samples?

	TOO LOW	ADEQUATE	TOO COLOURED
SAMPLE A			
SAMPLE B			
SAMPLE C			
SAMPLE D			
SAMPLE E			
SAMPLE F			
SAMPLE G			
SAMPLE H			

SAMPLE I			
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6. How do you find the sweetness (sugar) of following samples?

	NOT SWEET AT ALL	NOT SUFFICIENT	APPROPRIATE	TOO SWEET
SAMPLE A				
SAMPLE B				
SAMPLE C				
SAMPLE D				
SAMPLE E				
SAMPLE F				
SAMPLE G				
SAMPLE H				
SAMPLE I				

7. How do you find the acidity of following samples?

	NOT ACIDIC AT ALL	NOT SUFFICIENT	APPROPRIATE	TOO ACIDIC
SAMPLE A				
SAMPLE B				
SAMPLE C				
SAMPLE D				
SAMPLE E				
SAMPLE F				
SAMPLE G				
SAMPLE H				
SAMPLE I				

8. In which degree is the firmness of apricot in below samples?

	NOT FIRM ENOUGH	ADEQUATE	TOO FIRM
SAMPLE A			
SAMPLE B			
SAMPLE C			
SAMPLE D			
SAMPLE E			
SAMPLE F			
SAMPLE G			
SAMPLE H			
SAMPLE I			

9. What do you think about the ripeness of the sample?

	UNRIPE	MIDRIPE	RIPE	OVERLY RIPE
SAMPLE A				
SAMPLE B				
SAMPLE C				
SAMPLE D				
SAMPLE E				
SAMPLE F				
SAMPLE G				
SAMPLE H				
SAMPLE I				

10. Are you satisfied with the flavour of the following sample?

	NOT SATISFIED	WEAKLY SATISFIED	SATISFIED	VERY SATISFIED
SAMPLE A				
SAMPLE B				
SAMPLE C				
SAMPLE D				
SAMPLE E				
SAMPLE F				
SAMPLE G				
SAMPLE H				
SAMPLE I				

11. Classify the quality of the following samples on the basis of your satisfaction.

	NOT SATISFIED	WEAKLY SATISFIED	SATISFIED	VERY SATISFIED
SAMPLE A				
SAMPLE B				
SAMPLE C				
SAMPLE D				
SAMPLE E				
SAMPLE F				
SAMPLE G				
SAMPLE H				
SAMPLE I				

### Part 3: Consumer perception for taking inevitable steps to improve the quality of Apricots.

Questions 12 and 13 are to classify the consumer preferences for apricots.

Answer the following questions by numbering 1 to 6 as required by making 1 the most important priority followed by less important characteristics of apricots.

12. Apricots are good when they possess the qualities below:

TASTE	
FIRMNESS	
SIZE	
SHAPE	
AROMA	
COLOUR	

Answer the following questions by numbering 1 to 4 as required by making 1 the most important priority followed by less important characteristics of apricots.

13. Apricots are not good when they possess the qualities below:

WEAKLY ODOURED	
TOO FIRM	
NOT COLOURED	
MEALY	

Any other Comment on quality criteria of the samples

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### ACKNOWLEDGEMENT

Thank you for taking the time to fill in the questionnaire. You will remain anonymous. The main purpose is to gather information from a sample of consumers, in this case from untrained customers.

Should you have any queries or comments regarding this survey, you are welcome to contact us at [bmehta@utas.edu.au](mailto:bmehta@utas.edu.au).